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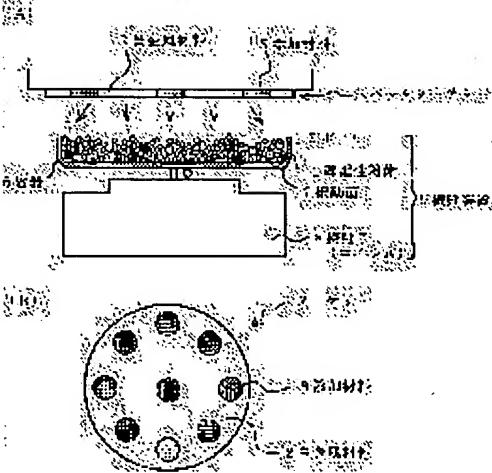
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(54) CONDUCTIVE CATALYST PARTICLE AND METHOD FOR MANUFACTURING THE SAME, GAS DIFFUSIVE CATALYST ELECTRODE AND ELECTROCHEMICAL DEVICE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide conductive catalyst particles which do not give rise to sintering and are excellent in catalyst characteristics and a method for manufacturing the same, a gas diffusive catalyst electrode and an electrochemical device.

SOLUTION: The conductive catalyst particles stuck with a catalyst material consists of an alloy of a noble metal material and an additive material of a thermally non-solid soluble system to the noble material on the surface of a conductive powder and the method for manufacturing comprises simultaneously bonding this noble metal material and additive material to the surface of the conductive powder by a physical vapor deposition process, the conductive catalyst particles stuck with the catalyst material consisting of the alloy of MI (wherein MI is noble metal elements, such as Pt, Ir, Pd, Rh, Au and Ru) and MII (wherein MII is Fe, Co, Ni, Cr, Al, Cu, Hf, Zr, Ti, V, Nb, Ta, W, Ga, Sn, Ge, Si, Re, Os, Pb, Bi, Sb,



Mo, Mn, O, N, F, C, Zn, In or rear earth elements) on the surface of the conductive powder, and the method for manufacturing such conductive catalyst particles is provided.

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CLAIMS

[Claim(s)]

[Claim 1] The conductive catalyst particle by which the noble-metals ingredient and the catalyst ingredient which consists of an alloy with the charge of add-in material of a non-dissolving system thermally to said noble-metals ingredient have adhered to the front face of conductive fine particles.

[Claim 2] The conductive catalyst particle which adheres to the alloy of said noble-metals ingredient and said charge of add-in material as said catalyst ingredient with physical vapor deposition and which was indicated to claim 1.

[Claim 3] The conductive catalyst particle whose charge of add-in material of said non-dissolving system is the ceramics and which was indicated to claim 1.

[Claim 4] The conductive catalyst particle whose charge of add-in material of said non-dissolving system is at least one sort in B (boron), silicon oxide, an oxidization gallium, a vanadium oxide, and tungstic oxide and which was indicated to claim 1.

[Claim 5] The conductive catalyst particle whose addition of the charge of add-in material of said non-dissolving system is 2-70-mol% or at % and which was indicated to claim 1.

[Claim 6] The conductive catalyst particle said whose physical vapor deposition is the spatter which uses said noble-metals ingredient and said charge of add-in material as a target and which was indicated to claim 2.

[Claim 7] The conductive catalyst particle said whose physical vapor deposition is the pulse laser deposition method and which was indicated to claim 2.

[Claim 8] The conductive catalyst particle by which the ion conductor has adhered to the front face of said conductive fine particles, and said catalyst ingredient has adhered to the front face of this ion conductor further and which was indicated to claim 1.

[Claim 9] The conductive catalyst particle which the coating weight of said catalyst ingredient indicated to said conductive fine particles to claim 1 which is 10 - 1000 % of the weight.

[Claim 10] The conductive catalyst particle whose electric resistance of said conductive fine particles is 10 to 3 or less ohm-m and which was indicated to claim 1.

[Claim 11] The conductive catalyst particle said whose conductive fine particles are at least one of carbon and ITO (Indium tin oxide: conductive oxide which doped tin to the indium oxide), and SnO₂ sorts and which was indicated to claim 1.

[Claim 12] The conductive catalyst particle which said conductive fine particles indicated to claim 1 whose specific surface area is the carbon more than 300m²/g.

[Claim 13] The conductive catalyst particle which said conductive fine particles indicated to claim 1 whose oil absorption is carbon (200ml / 100g or more).

[Claim 14] On the front face of conductive fine particles, MI (however, MI is at least one sort chosen from noble-metals elements, such as Pt, Ir, Pd, Rh, Au, and Ru.), MII (however, MII is at least one sort chosen from Fe, Co, nickel, Cr, aluminum, Cu, Hf, Zr, Ti, V, Nb, Ta, W, Ga, Sn, germanium, Si, Re, Os, Pb, Bi, Sb, Mo, Mn, O, N, F, C, Zn, In, and rare earth elements.) The conductive catalyst particle to which the catalyst ingredient which consists of an alloy has adhered.

[Claim 15] Said catalyst ingredient is a MI-MII'-MII" alloy (however, MI is at least one sort chosen from noble-metals elements, such as Pt, Ir, Pd, Rh, Au, and Ru.). MII' is at least one sort chosen from Fe, Co, nickel, Cr, aluminum, Sn, Cu, Mo, W, O, N, F, and C. MII" is at least one sort chosen from Hf, Zr, Ti, V, Nb, Ta, Ga, germanium, Si, Re, Os, Pb, Bi, Sb, Mn, and rare earth elements. from -- conductive catalyst particle which it became, and was indicated to claim 14 which is $a+b+c=100\text{at\%}$, $0.5\text{at\%}\leq b+c\leq 60\text{at\%}$, and $b\leq 60\text{at\%}$ and $c\leq 20\text{at\%}$ when the presentation was $\text{MIA-MII}'\text{b-MII}''\text{c}$.

[Claim 16] The conductive catalyst particle to which said catalyst ingredient has adhered with physical vapor deposition and which was indicated to claim 14.

[Claim 17] The conductive catalyst particle said whose physical vapor deposition is the spatter which uses said MI and said MII as a target and which was indicated to claim 16.

[Claim 18] The conductive catalyst particle said whose physical vapor deposition is the pulse laser deposition method and which was indicated to claim 16.

[Claim 19] The conductive catalyst particle by which the ion conductor has adhered to the front face of said conductive fine particles, and said catalyst ingredient has adhered to the front face of this ion conductor further and which was indicated to claim 14.

[Claim 20] The conductive catalyst particle which the coating weight of said catalyst ingredient indicated to said conductive fine particles to claim 14 which is 10 - 1000 % of the weight.

[Claim 21] The conductive catalyst particle whose electric resistance of said conductive fine particles is 10 to 3 or less ohm-m and which was indicated to claim 14.

[Claim 22] The conductive catalyst particle said whose conductive fine particles are at least one of carbon and ITO (Indium tin oxide: conductive oxide which doped tin to the indium oxide), and SnO₂ sorts and which was indicated to claim 14.

[Claim 23] The conductive catalyst particle which said conductive fine particles indicated to claim 14 whose specific surface area is the carbon more than 300m²/g.

[Claim 24] The conductive catalyst particle which said conductive fine particles indicated to claim 14 whose oil absorption is carbon (200ml / 100g or more).

[Claim 25] The gaseous diffusion nature catalyst electrode containing the conductive catalyst particle indicated in any 1 term of claims 1, 14, and 15.

[Claim 26] The gaseous diffusion nature catalyst electrode to which said conductive catalyst particle is bound with resin and which was indicated to claim 25.

[Claim 27] The gaseous diffusion nature catalyst electrode with which said conductive catalyst particle has adhered on a charge collector and which was indicated to claim 25.

[Claim 28] The electrochemistry device with which the gaseous diffusion nature catalyst electrode which consisted of at least two electrodes and an ion conductor pinched among these electrodes, and was indicated to claim 25 constitutes at least one of said electrodes.

[Claim 29] The electrochemistry device which is constituted as a fuel cell and which was indicated to claim 28.

[Claim 30] The electrochemistry device which is constituted as a hydrogen manufacturing installation and which was indicated to claim 28.

[Claim 31] The manufacture approach of a conductive catalyst particle of making the charge of add-in material of a non-dissolving system adhering to the front face of conductive fine particles with physical vapor deposition thermally to a noble-metals ingredient and said noble-metals ingredient at coincidence, and obtaining the conductive catalyst particle to which the catalyst ingredient which consists of an alloy of said noble-metals ingredient and said charge of add-in material by this comes to adhere.

[Claim 32] The manufacture approach of the conductive catalyst particle indicated to claim 31 of having the process which makes said charge of add-in material of a non-dissolving system adhering to the front face of said conductive fine particles with said physical vapor deposition thermally to said noble-metals ingredient and said noble-metals ingredient at coincidence while vibrating said conductive fine particles.

[Claim 33] The manufacture approach of the conductive catalyst particle which makes said noble-metals ingredient and said charge of add-in material adhere to the front face of said conductive fine particles

with said physical vapor deposition, vibrating both said conductive fine particles and an oscillating magnification means and which was indicated to claim 32.

[Claim 34] The manufacture approach of the conductive catalyst particle indicated to claim 33 to which is made to mix said conductive fine particles and said ball, and installs in the same container, using a ball as said oscillating magnification means, and said vibration is applied.

[Claim 35] The manufacture approach of a conductive catalyst particle which uses said ball as the ceramics with a diameter of 1-15mm or a metal ball and which was indicated to claim 34.

[Claim 36] The manufacture approach of the conductive catalyst particle which installs said component using the components formed so that it might be an abbreviation plane as said oscillating magnification means and the pattern of an abbreviation swirl, the shape of an approximately concentric circle, and the letter of an abbreviation cuff might be made so that at least a part may be in the condition of not fix at a container, arranges said conductive fine particles and applies said vibration on this component and which was indicated to claim 33.

[Claim 37] The manufacture approach of a conductive catalyst particle which makes said component formed in the pattern of an abbreviation swirl, the shape of an approximately concentric circle, and the letter of an abbreviation cuff a metal wire with a diameter of 1-10mm and which was indicated to claim 36.

[Claim 38] The manufacture approach of the conductive catalyst particle indicated to claim 36 which makes smaller about 5mm than the bore of said container the outer diameter of said component formed in the pattern of an abbreviation swirl, the shape of an approximately concentric circle, and the letter of an abbreviation cuff, and sets the pitch of a pattern to 5-15mm.

[Claim 39] The manufacture approach of the conductive catalyst particle indicated to claim 33 which makes the thickness or the path of said oscillating magnification means 10 - 70% to the thickness which said conductive fine particles make.

[Claim 40] The manufacture approach of a conductive catalyst particle for the distribution field of said conductive fine particles which makes the rate of surface ratio of said oscillating magnification means 30 - 80% and which was indicated to claim 33.

[Claim 41] The manufacture approach of a conductive catalyst particle which sets the frequency of said vibration to 5-200Hz and which was indicated to claim 32.

[Claim 42] The manufacture approach of a conductive catalyst particle which sets the amplitude of said vibration to **(0.5-20) mm and which was indicated to claim 32.

[Claim 43] MI (however, MI is at least one sort chosen from noble-metals elements, such as Pt, Ir, Pd, Rh, Au, and Ru.), MII (MII is at least one sort chosen from Fe, Co, nickel, Cr, aluminum, Cu, Hf, Zr, Ti, V, Nb, Ta, W, Ga, Sn, germanium, Si, Re, Os, Pb, Bi, Sb, Mo, Mn, O, N, F, C, Zn, In, and rare earth elements.) The manufacture approach of a conductive catalyst particle of obtaining the conductive catalyst particle to which make coincidence adhering to the front face of conductive fine particles with physical vapor deposition, and the catalyst ingredient which consists of said alloy of MI and said MII by this comes to adhere.

[Claim 44] The manufacture approach of the conductive catalyst particle which vibrates said conductive fine particles in case said MI and said MII are made to adhere to the front face of said conductive fine particles with said physical vapor deposition and which was indicated to claim 43.

[Claim 45] The manufacture approach of the conductive catalyst particle which makes said MI and said MII adhere to the front face of said conductive fine particles with said physical vapor deposition, vibrating both said conductive fine particles and an oscillating magnification means and which was indicated to claim 44.

[Claim 46] The manufacture approach of the conductive catalyst particle indicated to claim 45 to which is made to mix said conductive fine particles and said ball, and installs in the same container, using a ball as said oscillating magnification means, and said vibration is applied.

[Claim 47] The manufacture approach of a conductive catalyst particle which uses said ball as the ceramics with a diameter of 1-10mm or a metal ball and which was indicated to claim 46.

[Claim 48] The manufacture approach of the conductive catalyst particle which installs said component

using the components formed so that it might be an abbreviation plane as said oscillating magnification means and the pattern of an abbreviation swirl , the shape of an approximately concentric circle , and the letter of an abbreviation cuff might be made so that at least a part may be in the condition of not fix at a container , arranges said conductive fine particles and applies said vibration on this component and which was indicated to claim 45 .

[Claim 49] The manufacture approach of a conductive catalyst particle which makes said component formed in the pattern of an abbreviation swirl, the shape of an approximately concentric circle, and the letter of an abbreviation cuff a metal wire with a diameter of 1.6mm and which was indicated to claim 48.

[Claim 50] The manufacture approach of the conductive catalyst particle indicated to claim 48 which makes smaller about 5mm than the bore of said container the outer diameter of said component formed in the pattern of an abbreviation swirl, the shape of an approximately concentric circle, and the letter of an abbreviation cuff, and sets the pitch of a pattern to 5-15mm.

[Claim 51] The manufacture approach of the conductive catalyst particle indicated to claim 45 which makes the thickness or the path of said oscillating magnification means 10 - 70% to the thickness which said conductive fine particles make.

[Claim 52] The manufacture approach of a conductive catalyst particle for the distribution field of said conductive fine particles which makes the rate of surface ratio of said oscillating magnification means 30 - 80% and which was indicated to claim 45.

[Claim 53] The manufacture approach of a conductive catalyst particle which sets the frequency of said vibration to 5-200Hz and which was indicated to claim 44.

[Claim 54] The manufacture approach of a conductive catalyst particle which sets the amplitude of said vibration to **(0.5-20) mm and which was indicated to claim 44.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a conductive catalyst particle and its manufacture approach, a gaseous diffusion nature catalyst electrode, and an electrochemistry device.

[0002]

[Description of the Prior Art] the catalyst particle with which, as for the gaseous diffusion nature catalyst electrode, the platinum as a catalyst ingredient is conventionally supported by the carbon as conductive fine particles -- the fluororesin and ion conductor as water-repellent resin -- the shape of a sheet -- fabricating (JP,5-36418,A) -- or pass the process applied on a carbon sheet -- it is manufactured.

[0003] When this electrode is used as an electrode for hydrocracking which constitutes fuel cells, such as a polymer electrolyte fuel cell, the proton (H⁺) produced by a fuel being ionized, and the produced electron being transmitted to conductive carbon, and flowing with catalyst ingredients, such as platinum, and ionizing hydrogen flows on the ionic conduction film through an ion conductor. Here, catalyst ingredients, such as platinum for ionizing the ion conductor and fuel, and oxidizer which let the gap which lets gas pass, the carbon which conducts the electrical and electric equipment, and ion pass, are needed.

[0004] Usually, as an approach of making platinum (catalyst ingredient) adhering to the front face of the carbon fine particles as conductive fine particles, platinum is ionized first, as liquefied, platinum is made to adhere to carbon fine particles by carbon being immersed in the solution containing this platinum, it is performing reduction and heat treatment subsequently, and there is the approach of making it adhere as particle platinum on the front face of carbon fine particles (patent No. 2879649).

[0005]

[Processes leading to Invention] However, in order that the conventional approach which was mentioned above may make platinum support on carbon fine particles, when it is required to perform reduction and heat treatment, for example, the temperature in this heat treatment is low, the crystallinity of platinum worsens and it is holding the trouble that a good catalyst property cannot be acquired.

[0006] Moreover, the proton (H⁺) produced by a fuel being ionized, and the produced electron being transmitted to conductive carbon, and flowing with catalyst ingredients, such as platinum which was mentioned above, and ionizing hydrogen flows on the ionic conduction film through an ion conductor. Therefore, since carbon fine particles and an ion conductor need to touch, after they support platinum to carbon fine particles, they usually apply an ion conductor. However, since platinum functions only in the part which touched gas, the platinum whose contact section with gas was lost with the ion conductor does not function.

[0007] After applying an ion conductor to carbon fine particles instead of this, there is a method of making platinum support. However, it must heat-treat in order to make the crystallinity of platinum good, but if an ion conductor is generally heated to the heat treatment temperature which makes the crystallinity of platinum good since thermal resistance is low, an ion conductor will deteriorate.

[0008] Drawing 24 (A) is the outline sectional view showing the conductive catalyst particle which the

carbon fine particles 1 are made to support platinum 27 with the conventional manufacture approach, and is obtained by it, and drawing 24 (B) is the outline sectional view showing the conductive catalyst particle which is made to support platinum 27 and is further obtained on it, after making an ion conductor 11 adhere to the carbon fine particles 1.

[0009] Since platinum 27 is spherical and exists on the front face of the carbon fine particles 1, it is easy to separate platinum 27 from on the front face of the carbon fine particles 1, and the conductive catalyst particle which supported the platinum obtained from the liquid phase needs many amounts of platinum in a production process, so that more clearly than drawing 24 (A). Furthermore, since platinum 27 is spherical and exists, only the front face of platinum 27 functions as a catalyst ingredient, and the interior does not function, but the effectiveness of catalyst ability is low to the amount of platinum. Moreover, although the illustration abbreviation was carried out, platinum 27 will enter also into the pore which exists on the front face of the carbon fine particles 1. For this reason, the platinum 27 which does not function effectively also exists and the effectiveness of catalyst ability is low to the amount of platinum. [0010] Moreover, when making platinum 27 support after applying an ion conductor 11 to carbon fine particles, as shown in drawing 24 (B), as mentioned above, heat treatment for making the crystallinity of platinum 27 good is needed, but if an ion conductor 11 generally has low thermal resistance and it heats to the heat treatment temperature which makes the crystallinity of platinum 27 good, an ion conductor 11 will deteriorate.

[0011] this invention persons proposed the gaseous diffusion nature catalyst electrode which has a good catalysis in the application for patent No. 293517 [2000 to] in the smaller amount of catalysts, as a result of inquiring wholeheartedly that a trouble which was mentioned above should be solved.

[0012] That is, according to invention concerning an application for patent No. (a prior invention is called hereafter.) 293517 [2000 to], the conductive catalyst particle by which platinum 27 adhered to the front face of the carbon fine particles 1 as shown in drawing 25 can be obtained using physical vapor deposition, such as a spatter as shown in drawing 25 , by making platinum (catalyst ingredient) adhere to the front face of the carbon fine particles (conductive fine particles) 1.

[0013] Namely, if physical vapor deposition is used as shown in drawing 26 (A), as for the conductive catalyst particle obtained by this, platinum 27 will have adhered only to the front face of the carbon fine particles 1. Therefore, since a good catalysis can be obtained in a smaller amount and the touch area of platinum 27 and gas is fully secured, the specific surface area of the platinum 27 contributed to a reaction becomes large, and catalyst ability also improves.

[0014] Moreover, platinum 27 can be made to adhere, without it becoming unnecessary to perform heat treatment for making the crystallinity of platinum good like before, and spoiling the engine performance of an ion conductor 11, since platinum 27 is made to adhere with physical vapor deposition even if it makes an ion conductor 11 adhere to the front face of the carbon fine particles 1 and makes platinum 27 adhere to it with physical vapor deposition on the front face of this ion conductor 11 further as shown in drawing 26 (B).

[0015]

[Problem(s) to be Solved by the Invention] However, this invention persons found out that it had the point which should be improved although a prior invention has the above-mentioned outstanding features.

[0016] In case a catalyst ingredient is made to adhere to the front face of conductive fine particles with physical vapor deposition, such as a spatter, when using a catalyst ingredient with high purity for it as a target, as compared with the chemical adhesion approach by the conventional technique which was mentioned above, a catalyst ingredient with very high purity can be adhered to it. However, when the purity of the catalyst ingredient adhering to the front face of conductive fine particles was high, there was a trouble that became easy to produce sintering between catalyst particles by the temperature rise, and activity fell by this sintering with the passage of time during the use as a fuel cell although early catalytic activity is high. And when the gaseous diffusion nature catalyst electrode containing a conductive catalyst particle with the high purity of a catalyst ingredient was used for a fuel cell, the trouble that an output declined by this sintering was also held.

[0017] Moreover, catalytic activity becomes high, so that a catalyst ingredient has a small particle size of the crystal grain. Although the initial particle size of the catalyst ingredient in physical vapor deposition was determined in the time of adhesion in conductive fine particles, when the purity of a catalyst ingredient was high, it was holding the trouble that the diameter of crystal grain tends to become large. For this reason, in order to acquire catalytic activity with it, detailed-ization of the diameter of crystal grain of a catalyst ingredient needed to be considered. [the high and purity of a catalyst ingredient, and] [high]

[0018] It is in providing with an electrochemistry device the conductive catalyst particle which this invention was made in order to improve the inadequate point, employing efficiently the features of the prior invention mentioned above, sintering did not generate the purpose, and was excellent in the catalyst property and its manufacture approach, a gaseous diffusion nature catalyst electrode and its manufacture approach, and a list.

[0019]

[Means for Solving the Problem] As a result of inquiring wholeheartedly that a trouble which was mentioned above should be solved, in order for this invention persons to prevent sintering of a catalyst ingredient In order to prevent the internal self-diffusion of the crystal lattice of a catalyst ingredient and to prevent this internal self-diffusion If the matter of a non-dissolving system which does not make an alloy with heating with a noble-metals ingredient, either is originally compulsorily introduced into the crystal lattice of a noble-metals ingredient and this is used as a catalyst ingredient, the sintering prevention effectiveness will be acquired, Moreover, a header and this invention were reached [that growth of the particle size of the catalyst ingredient at the time of adhesion is controlled, and catalytic activity becomes good as a result also about detailed-ization of the crystal grain of a catalyst ingredient by introducing the matter of a non-dissolving system compulsorily into the crystal lattice of a noble-metals ingredient, and].

[0020] Namely, the catalyst ingredient with which this invention becomes the front face of conductive fine particles from an alloy with the charge of add-in material of a non-dissolving system thermally to a noble-metals ingredient and said noble-metals ingredient has adhered. A conductive catalyst particle is started (the 1st conductive catalyst particle of this invention is called hereafter.). Moreover, the charge of add-in material of a non-dissolving system is made to adhere to the front face of conductive fine particles with physical vapor deposition thermally at coincidence to the noble-metals ingredient and said noble-metals ingredient for manufacturing this conductive catalyst particle. The manufacture approach of a conductive catalyst particle of obtaining the conductive catalyst particle to which the catalyst ingredient which consists of an alloy of said noble-metals ingredient and said charge of add-in material by this comes to adhere is started (the manufacture approach of the 1st conductive catalyst particle of this invention is called hereafter.).

[0021] Moreover, the gaseous diffusion nature catalyst electrode containing the conductive catalyst particle by which the noble-metals ingredient and the catalyst ingredient which consists of an alloy with the charge of add-in material of a non-dissolving system thermally to said noble-metals ingredient have adhered to the front face of conductive fine particles is started (the 1st gaseous diffusion nature catalyst electrode of this invention is called hereafter.).

[0022] Since said charge of add-in material of a non-dissolving system is made to adhere to the front face of said conductive fine particles with said physical vapor deposition thermally to said noble-metals ingredient and said noble-metals ingredient at coincidence according to invention of the 1st of this invention Properly speaking, said charge of add-in material of a non-dissolving system which does not make an alloy with heating with said noble-metals ingredient, either It can introduce compulsorily into the crystal lattice of said noble-metals ingredient, and the conductive catalyst particle by which said catalyst ingredient which consists of an alloy of said noble-metals ingredient and said charge of add-in material comes to adhere to the front face of said conductive fine particles can be obtained. Since this conductive catalyst particle contains said charge of add-in material in said catalyst ingredient, the internal self-diffusion of the crystal lattice of said noble-metals ingredient in said catalyst ingredient is prevented, and **** sintering mentioned already cannot generate it easily. In addition, by the chemical

adhesion approach by the conventional technique, said charge of add-in material of a non-dissolving system cannot be introduced into said noble-metals ingredient, and cannot obtain said alloy.

[0023] Moreover, since said charge of add-in material of a non-dissolving system is made to adhere to the front face of said conductive fine particles with said physical vapor deposition thermally to said noble-metals ingredient and said noble-metals ingredient at coincidence, growth of the particle size of said noble-metals ingredient at the time of adhesion is controlled, and it has the outstanding catalytic activity.

[0024] Furthermore, since said catalyst ingredient is made to adhere to the front face of said conductive fine particles with said physical vapor deposition At low temperature, the 1st conductive catalyst particle of this invention which can adhere to the front face of said conductive fine particles, and is obtained a crystalline good catalyst ingredient Since a good catalysis can be obtained in said smaller amount of catalyst ingredients and the touch area of said catalyst ingredient and gas is fully secured, the specific surface area of said catalyst ingredient contributed to a reaction becomes large, and catalyst ability also improves.

[0025] This invention on the front face of conductive fine particles Moreover, MI (however, MI is at least one sort chosen from noble-metals elements, such as Pt, Ir, Pd, Rh, Au, and Ru.), MII (however, MII is at least one sort chosen from Fe, Co, nickel, Cr, aluminum, Cu, Hf, Zr, Ti, V, Nb, Ta, W, Ga, Sn, germanium, Si, Re, Os, Pb, Bi, Sb, Mo, Mn, O, N, F, C, Zn, In, and rare earth elements.) The conductive catalyst particle to which the catalyst ingredient which consists of an alloy has adhered is started (the 2nd conductive catalyst particle of this invention is called hereafter.). Moreover, the manufacture approach of a conductive catalyst particle of obtaining the conductive catalyst particle to which make said MI and said MII adhering to the front face of conductive fine particles with physical vapor deposition at coincidence, and the catalyst ingredient which consists of said alloy of MI and said MII by this comes to adhere is started (the manufacture approach of the 2nd conductive catalyst particle of this invention is called hereafter.).

[0026] Moreover, the gaseous diffusion nature catalyst electrode containing the conductive catalyst particle by which the catalyst ingredient which serves as said MI from an alloy with said MII has adhered to the front face of conductive fine particles is started (the 2nd gaseous diffusion nature catalyst electrode of this invention is called hereafter.).

[0027] According to invention of the 2nd of this invention, since said MI and said MII are made to adhere to the front face of said conductive fine particles with said physical vapor deposition at coincidence, said MII can be compulsorily introduced into the crystal lattice of said MI, and the conductive catalyst particle by which said catalyst ingredient which consists of said alloy of MI and said MII comes to adhere to the front face of said conductive fine particles can be obtained. Since this conductive catalyst particle contains said MII in said catalyst ingredient, the movement toward transition of said MI in said catalyst ingredient is checked, the internal self-diffusion of a crystal lattice is prevented, and it can prevent generating of **** sintering mentioned already.

[0028] Moreover, since said catalyst ingredient is made to adhere to the front face of said conductive fine particles with said physical vapor deposition At low temperature, the 2nd conductive catalyst particle of this invention which can adhere to the front face of said conductive fine particles, and is obtained a crystalline good catalyst ingredient Since a good catalysis can be obtained in said smaller amount of catalyst ingredients and the touch area of said catalyst ingredient and gas is fully secured, the specific surface area of said catalyst ingredient contributed to a reaction becomes large, and catalyst ability also improves.

[0029] Moreover, this invention consists of at least two electrodes and an ion conductor pinched among these electrodes, and requires the 1st gaseous diffusion nature electrode of this invention or the 2nd gaseous diffusion nature electrode mentioned above for the electrochemistry device which constitutes at least one of said electrodes.

[0030] According to the electrochemistry device of this invention, since the 1st [of this invention] or 2nd above-mentioned gaseous diffusion nature catalyst electrode constitutes at least one of said electrodes, generating of sintering can be prevented, good output characteristics are obtained, and these

output characteristics can be maintained over a long time.

[0031]

[Embodiment of the Invention] Hereafter, based on the gestalt of operation, this invention is explained still more concretely.

[0032] In the 1st manufacture approach based on this invention, it is desirable to apply the spatter using the target which consists of said noble-metals ingredient and said charge of add-in material as said physical vapor deposition. Said spatter can be produced easily, and is high, and is good. [of membrane formation nature] [of productivity]

[0033] Moreover, the pulse laser deposition method other than said spatter may be applied as said physical vapor deposition. The control in membrane formation is easy for said pulse laser deposition method, and it is good. [of membrane formation nature]

[0034] By the chemical adhesion approach by the conventional technique mentioned above, said charge of add-in material of a non-dissolving system cannot be introduced into said noble-metals ingredient, and cannot obtain said catalyst ingredient which consists of said alloy. On the other hand, the 1st manufacture approach based on this invention Since said charge of add-in material of a non-dissolving system is made to adhere to the front face of said conductive fine particles with said physical vapor deposition, such as said spatter, thermally to said noble-metals ingredient and said noble-metals ingredient at coincidence Properly speaking, with said noble-metals ingredient, said charge of add-in material of a non-dissolving system which does not make an alloy with heating, either can be compulsorily introduced into the crystal lattice of said noble-metals ingredient. Since the internal self-diffusion of the crystal lattice of said noble-metals ingredient is prevented by said charge of add-in material, sintering cannot generate the 1st [based on this invention which can obtain the conductive catalyst particle by which said catalyst ingredient which consists of an alloy of said noble-metals ingredient and said charge of add-in material comes to adhere to the front face of said conductive fine particles, and contains this conductive catalyst particle by this] gaseous diffusion nature catalyst electrode much more easily.

[0035] Moreover, since the 1st [based on this invention] conductive catalyst particle makes said charge of add-in material of a non-dissolving system adhere to the front face of said conductive fine particles with said physical vapor deposition, such as said spatter, thermally to said noble-metals ingredient and said noble-metals ingredient at coincidence, growth of the particle size of said noble-metals ingredient at the time of adhesion is controlled more, and it has the further excellent catalytic activity.

[0036] Furthermore, by said spatter or the pulse laser deposition method, since said catalyst ingredient is made to adhere At low temperature, the 1st [based on this invention which can adhere to the front face of said conductive fine particles, and is obtained] conductive catalyst particle a crystalline good catalyst ingredient Since a good catalysis can be obtained in said smaller amount of catalyst ingredients and the touch area of said catalyst ingredient and gas is fully secured, the specific surface area of said catalyst ingredient contributed to a reaction becomes large, and catalyst ability can also improve.

[0037] Here, in Patent Publication Heisei 11-510311, although the example which carries out spatter membrane formation of the noble metals on a carbon sheet is indicated, since said catalyst ingredient is made to adhere to the front face of the fine particles which have conductivity, the 1st manufacture approach based on this invention can enlarge more specific surface area of said catalyst ingredient contributed to a reaction compared with said Patent Publication Heisei 11-510311, and can aim at improvement in catalyst ability.

[0038] In order to prevent sintering more effectively, as for the addition of the charge of add-in material of said non-dissolving system, it is desirable that it is 2-70-mol% or at %. Since there are too few additions of said charge of add-in material, when in the case of two-mol% or below at% the effectiveness of sintering prevention may fall and 70 mols or at% is exceeded, since there are too many additions of said charge of add-in material, catalytic activity may become poor.

[0039] It is desirable to use the ceramics as a charge of add-in material of said non-dissolving system, and, specifically, it is desirable to use at least one sort in the silicon oxide of B (boron), SiO, and SiO₂ grade, the oxidization gallium of Ga₂O₃ grade, the vanadium oxide of V₂O₅ grade, and the tungstic

oxide of WO₃ grade.

[0040] As opposed to said noble-metals ingredient and said noble-metals ingredient thermally said charge of add-in material of a non-dissolving system on the front face of said conductive fine particles In case it is made to adhere with said physical vapor deposition, such as said spatter, it is desirable to vibrate said conductive fine particles. Moreover, said conductive fine particles, It is more desirable to make said noble-metals ingredient and said charge of add-in material adhere to the front face of said conductive fine particles with said physical vapor deposition, arranging an oscillating magnification means on a plane of vibration, and vibrating these. Thereby, it vibrates more, and is fully mixed and stopping of said conductive fine particles at one on said plane of vibration is lost. Therefore, not only the front face of a powder bed but an internal thing can come out of said conductive fine particles to a front face, and said catalyst ingredient which consists of an alloy of said noble-metals ingredient and said charge of add-in material can be made to adhere to homogeneity further to said all conductive fine particles.

[0041] Drawing 1 is the outline sectional view of an example of the manufacturing installation of the 1st [based on this invention] conductive catalyst particle.

[0042] As shown in drawing 1 (A), as said physical vapor deposition on the front face of the conductive fine particles 1 by for example, said spatter using the target 4 which consists of a noble-metals ingredient 2 and a charge 3 of add-in material in case said catalyst ingredient is made to adhere, a front face mixes the conductive fine particles 1 and a ball 5 using the smooth ball 5 as said oscillating magnification means -- making -- the plane-of-vibration 7 top in the same container 6 -- arranging -- for example, electromagnetism -- it is desirable to apply said vibration with the vibrator 8 which consists of a coil type or an ultrasonic horn. Thus, by using the constituted rocking equipment 9, it floods each other, and mixes and flows and the thing of the conductive fine particles 1 which fly ball 5 and to stop at one on a plane of vibration 7 is lost. And not only the front face of the powder bed of the conductive fine particles 1 but an internal thing will come out to a front face, and can make said catalyst ingredient adhere to homogeneity more to the conductive whole fine particles 1 by said spatter within a container 6.

[0043] In this case, as for a ball 5, it is desirable that they are the ceramics with a diameter of 1-15mm or a metal ball.

[0044] As shown in drawing 1 (B), moreover, a target 4 As opposed to the noble-metals ingredient 2 The silicon oxide of B (boron), SiO, and SiO₂ grade, It is desirable to have the structure where the charges 3 of add-in material, such as an oxidization gallium of Ga₂O₃ grade, a vanadium oxide of V₂O₅ grade, and tungstic oxide of WO₃ grade, were introduced. It is possible to introduce the charge 3 of add-in material compulsorily into the crystal lattice of the noble-metals ingredient 2 with said physical vapor deposition, such as said spatter using such a target 4.

[0045] As the 1st [based on this invention] conductive catalyst particle is shown in drawing 2 (A), the catalyst ingredient 10 which consists of an alloy of said noble-metals ingredient and said charge of add-in material has adhered to the front face of the conductive fine particles 1. The internal self-diffusion in the crystal lattice of said noble-metals ingredient is effectively prevented by said charge of add-in material, and the 1st [based on this invention containing this conductive catalyst particle] gaseous diffusion nature catalyst electrode can prevent generating of sintering further by it.

[0046] Moreover, since said charge of add-in material can control growth of the particle size of said noble-metals ingredient at the time of adhesion on the front face of said conductive fine particles, the 1st [based on this invention] conductive catalyst particle has the outstanding catalytic activity.

[0047] Furthermore, since a good catalysis can be obtained in catalyst ingredient 10 smaller amount and the touch area of the catalyst ingredient 10 and gas is fully secured, the specific surface area of the catalyst ingredient 10 contributed to a reaction becomes large, and catalyst ability also improves.

[0048] Moreover, as shown in drawing 2 (B), the catalyst ingredient 10 which consists of an alloy of said noble-metals ingredient and said charge of add-in material may adhere to the front face of the conductive fine particles 1 at the ununiformity, and it has the same outstanding property as the 1st [based on this invention which has the structure of drawing 2 (A)] conductive catalyst particle even in

this case.

[0049] Furthermore, an ion conductor 11 is made to adhere to the front face of the conductive fine particles 1, as shown in drawing 2 (C). Furthermore, since the catalyst ingredient 10 which consists of an alloy of said noble-metals ingredient and said charge of add-in material with said physical vapor deposition can be made to adhere to the front face of this ion conductor 11. The catalyst ingredient 10 can be made to adhere, without it becoming unnecessary to perform heat treatment for making the crystallinity of a catalyst good like before, and spoiling the engine performance of an ion conductor 11.

[0050] When the 1st [based on which this invention of (A) shown in drawing 2 , (B) and (C)] conductive catalyst particle also demonstrates both catalyst ability and conductivity, it is desirable to make the catalyst ingredient 10 adhere at 10 - 1000% of the weight of a rate to the conductive fine particles 1, and Pt, Ir, Rh, etc. are mentioned as said noble-metals ingredient.

[0051] It is desirable to, apply the spatter using the target which consists of said MI and said MII as said physical vapor deposition in the 2nd manufacture approach based on this invention on the other hand. Said spatter can be produced easily, and is high, and is good. [of membrane formation nature] [of productivity]

[0052] Moreover, the pulse laser deposition method other than said spatter may be applied as said physical vapor deposition. The control in membrane formation is easy for said pulse laser deposition method, and it is good. [of membrane formation nature]

[0053] By the chemical adhesion approach by the conventional technique mentioned above, said MII will be introduced [be / it / under / said MI / receiving] by diffusion by heating, and particle size will usually increase by sintering in the case of such heating. On the other hand, since the 2nd manufacture approach based on this invention makes said MI and said MII adhere to the front face of said conductive fine particles with said physical vapor deposition, such as said spatter, at coincidence, it can introduce said MII compulsorily, without heating into the crystal lattice of said MI. Since the internal self-diffusion of the crystal lattice of said MI is prevented by said MII, sintering cannot generate the 2nd [based on this invention which can obtain the conductive catalyst particle by which said catalyst ingredient which consists of said alloy of MI and said MII comes to adhere to the front face of said conductive fine particles, and contains this conductive catalyst particle by this] gaseous diffusion nature catalyst electrode much more easily.

[0054] Furthermore, by said spatter or the pulse laser deposition method, since said catalyst ingredient is made to adhere At low temperature, the 2nd [based on this invention which can adhere to the front face of said conductive fine particles, and is obtained] conductive catalyst particle a crystalline good catalyst ingredient Since a good catalysis can be obtained in said smaller amount of catalyst ingredients and the touch area of said catalyst ingredient and gas is fully secured, the specific surface area of said catalyst ingredient contributed to a reaction becomes large, and catalyst ability can also improve.

[0055] Here, in Patent Publication Heisei 11-510311, although the example which carries out spatter membrane formation of the noble metals on a carbon sheet is indicated, since said catalyst ingredient is made to adhere to the front face of the fine particles which have conductivity, the 2nd manufacture approach based on this invention can enlarge more specific surface area of said catalyst ingredient contributed to a reaction compared with said Patent Publication Heisei 11-510311, and can aim at improvement in catalyst ability.

[0056] About said catalyst ingredient, it is a MI-MII'-MII" alloy (however, MI is at least one sort chosen from noble-metals elements, such as Pt, Ir, Pd, Rh, Au, and Ru.). MII' is at least one sort chosen from Fe, Co, nickel, Cr, aluminum, Sn, Cu, Mo, W, O, N, F, and C. MII" Hf, Zr, Ti, V, Nb, Ta, Ga, germanium, Si, it is at least one sort chosen from Re, Os, Pb, Bi, Sb, Mn, and rare earth elements. Since it has the catalyst ability which prevented sintering more effectively and was more excellent when carrying out and making the presentation into MIa-MII'b-MII"c It is more desirable to consider as $c \leq 20\text{at\%}$ $b \leq 60\text{at\%}$ $a+b+c=100\text{at\%}$ and $0.5\text{at\%} \leq b+c \leq 60\text{at\%}$.

[0057] When the value of said $b+c$ is less than [0.5at\%], since there are too few additions of said MII' and said MII", the sintering prevention effectiveness may decrease. Moreover, when exceeding 60at\% , since there are too many additions of said MII' and said MII", a catalysis tends to fall, and when

the 2nd [based on this invention containing this conductive catalyst particle] gaseous diffusion nature catalyst electrode is used for a fuel cell, an output may decline.

[0058] Moreover, as for the addition of said MII' (at least one sort chosen from Fe, Co, nickel, Cr, aluminum, Sn, Mo, Cu, W, O, N, F, and C) as MII, it is desirable that it is less than [60at%], and within the limits of this, while a better catalysis is obtained, the more effective sintering prevention effectiveness is acquired. Moreover, it is also possible to improve catalytic activity more. When exceeding 60at(s)%, since there are too many additions of said MII', a catalysis tends to fall, and an output may decline.

[0059] Furthermore, in order to acquire a better catalysis and the more effective sintering prevention effectiveness, as for the addition of said MII" (at least one sort chosen from Hf, Zr, Ti, V, Nb, Ta, B, Ga, Si, Re, Os, Pb, Bi, Sb, Mn, and rare earth elements) as MII, it is desirable that it is less than [20at%]. When 20at(s)% is exceeded, since there are too many additions, catalytic activity tends to become poor, and an output may decline.

[0060] In case said MI and said MII are made to adhere to the front face of said conductive fine particles with said physical vapor deposition, such as said spatter, it is desirable to vibrate said conductive fine particles, and it is more desirable to make said MI and said MII adhere to the front face of said conductive fine particles with said physical vapor deposition, arranging said conductive fine particles and an oscillating magnification means on a plane of vibration, and vibrating these. Thereby, it vibrates more, and is fully mixed and stopping of said conductive fine particles at one on said plane of vibration is lost. Therefore, not only the front face of a powder bed but an internal thing can come out of said conductive fine particles to a front face, and said catalyst ingredient which consists of said alloy of MI and said MII can be made to adhere to homogeneity further to said all conductive fine particles.

[0061] Drawing 3 is the outline sectional view of an example of the manufacturing installation of the 2nd [based on this invention] conductive catalyst particle.

[0062] As shown in drawing 3 (A), as said physical vapor deposition on the front face of the conductive fine particles 1 by for example, said spatter using the target 4 which consists of MI12 and MII13 in case said catalyst ingredient is made to adhere, a front face mixes the conductive fine particles 1 and a ball 5 using the smooth ball 5 as said oscillating magnification means -- making -- the plane-of-vibration 7 top in the same container 6 -- arranging -- for example, electromagnetism -- it is desirable to apply said vibration with the vibrator 8 which consists of a coil type or an ultrasonic horn. Thus, by using the constituted rocking equipment 9, it floods each other, and mixes and flows and the thing of the conductive fine particles 1 which fly ball 5 and to stop at one on a plane of vibration 7 is lost. And not only the front face of the powder bed of the conductive fine particles 1 but an internal thing will come out to a front face, and can make said catalyst ingredient adhere to homogeneity more to the conductive whole fine particles 1 by said spatter within a container 6.

[0063] In this case, as for a ball 5, it is desirable that they are the ceramics with a diameter of 1-10mm or a metal ball.

[0064] Moreover, as shown in drawing 3 (B), as for a target 4, it is desirable to have the structure where MII13 was introduced to MI12, and it can introduce MII13 compulsorily only with said physical vapor deposition, such as said spatter using such a target 4, without heating in the crystal lattice of MI12.

[0065] As the 2nd [based on this invention] conductive catalyst particle is shown in drawing 4 (A), the catalyst ingredient 14 which consists of said alloy of MI and said MII has adhered only to the front face of the conductive fine particles 1. The internal self-diffusion in the crystal lattice of said MI is effectively prevented by said MII, and the 2nd [based on this invention containing this conductive catalyst particle] gaseous diffusion nature catalyst electrode can prevent generating of sintering further by it.

[0066] Moreover, since a good catalysis can be obtained in catalyst ingredient 14 smaller amount and the touch area of the catalyst ingredient 14 and gas is fully secured, the specific surface area of the catalyst ingredient 14 contributed to a reaction becomes large, and catalyst ability also improves.

[0067] Moreover, as shown in drawing 4 (B), the catalyst ingredient 14 which consists of said alloy of MI and said MII may adhere to the front face of the conductive fine particles 1 at the ununiformity, and

it has the same outstanding property as the 2nd [based on this invention which has the structure of drawing 4 (A)] conductive catalyst particle even in this case.

[0068] Furthermore, the catalyst ingredient 14 can be made to adhere, without it becoming unnecessary to perform heat treatment for making the crystallinity of a catalyst good like before, and spoiling the engine performance of an ion conductor 11, since an ion conductor 11 can be made to be able to adhere to the front face of the conductive fine particles 1 and the catalyst ingredient 14 which consists of said alloy of MI and said MII with said physical vapor deposition can be made to adhere to the front face of this ion conductor 11 further as shown in drawing 4 (C).

[0069] It is desirable that the 2nd [based on which this invention of (A) shown in drawing 4 , (B), and (C)] conductive catalyst particle also makes the catalyst ingredient 14 adhere at 10 - 1000% of the weight of a rate to the conductive fine particles 1 when demonstrating both catalyst ability and conductivity.

[0070] Drawing 5 is the schematic diagram of the container 6 which has arranged the ball 5 as the conductive fine particles 1 by the manufacture approach and said oscillating magnification means of the 1st [based on this invention], or 2nd conductive catalyst particle.

[0071] As shown in drawing 5 , it is desirable to make the ratio of the gross area A of a ball 5 to the area S of the distribution field of the conductive fine particles 1 into 30 - 80%. If this ratio is too small, if too large, mixing [of the conductive fine particles 1] will become inadequate, and the rate of the conductive fine particles 1 becomes small, and the deposit efficiency of said catalyst ingredient by said spatter will worsen, and will become inadequate [the productive efficiency of the catalyst particle to which said catalyst ingredient adhered].

[0072] some containers 6 which have arranged the ball 5 as the conductive fine particles 1 and said oscillating magnification means to drawing 6 -- it is desirable to make the path R of the ball 5 as said oscillating magnification means into 10 - 70% to the thickness t which the conductive fine particles 1 make so that an expansion outline sectional view may be shown. This path becomes disadvantageous by the same reason as that case where it is the above-mentioned rate of surface ratio as it is out of range.

[0073] Moreover, in order for the frequency of said vibration given to the ball 5 as the conductive fine particles 1 and said oscillating magnification means with a trembler 8 to mix the conductive fine particles 1 more than enough, since it is desirable that it is 5-200Hz and the amplitude of said vibration also has it, it is desirable that it is **(0.5-20) mm (also in case of the same as when it is [the following and] the gestalt of other operations). [same]

[0074] Under the environment of monograph affair [which was mentioned above] within the limits which is made desirable, if said catalyst ingredient is made to adhere to the front face of said conductive fine particles by said spatter for example, since said conductive fine particles can carry out much more good vibration, they can be further adhered to the front face of said conductive fine particles in said catalyst ingredient at homogeneity. when it separates from each above-mentioned range (i.e., when the path of said ball is less than 1mm), when exceeding 15mm and said vibration frequency is less than 5Hz, or when exceeding 200Hz When said amplitude is less than **0.5mm, as for said conductive fine particles, good vibration cannot be carried out, but said conductivity [having piled up in the pars basilaris ossis occipitalis of said container, without flowing] fine particles arise, and uniform membrane formation becomes impossible. Moreover, when said amplitude exceeds 20mm, there is a possibility that said conductive fine particles may jump out, and yield may decrease.

[0075] The 1st or 2nd manufacture approach based on this invention is replaced with said ball. As said oscillating magnification means Are an abbreviation plane and the components formed so that the pattern of an abbreviation swirl, the shape of an approximately concentric circle, and the letter of an abbreviation cuff might be made are used. Said component is installed so that at least a part may be in the condition of not fixing in a container (that is, itself vibrates freely in three dimensions like below : the same), on this component, said conductive fine particles may be arranged and said vibration may be applied.

[0076] As said oscillating magnification means, drawing 7 is an abbreviation plane and is the schematic diagram of rocking equipment usable to the 1st or 2nd manufacture approach based on this invention

using the components 15 formed so that an abbreviation swirl-like pattern might be made.

[0077] As said oscillating magnification means, drawing 8 is an abbreviation plane and is the outline sectional view of rocking equipment usable to the 1st or 2nd manufacture approach based on this invention using the components (namely, connected in the direction of a path) 16 formed so that an approximately concentric circle-like pattern might be made.

[0078] As said oscillating magnification means, drawing 9 is an abbreviation plane and is the outline sectional view of rocking equipment usable to the 1st or 2nd manufacture approach based on this invention using the components 17 formed so that the pattern of the letter of an abbreviation cuff might be made.

[0079] If in any [which is shown in drawing 7 - drawing 9] case said components 15 and 16 or 17 is installed so that it may be in the condition of not fixing at some containers [at least] 6, and the conductive fine particles 1 are arranged and said vibration is applied on these components 15 and 16 or 17 Since components 15 and 16 or the configuration of 17 vibrates while it had been held, the conductive fine particles 1 can vibrate further and can flow to fitness more. If said catalyst ingredient is adhered to the front face of the conductive fine particles 1 with said physical vapor deposition, such as said spatter, at this time, the conductive fine particles 1 in a container 6 can be crossed to the whole not only including that front face but including an internal thing, and can adhere said catalyst ingredient to homogeneity.

[0080] Said component formed in the pattern of an abbreviation swirl, the shape of an approximately concentric circle, and the letter of an abbreviation cuff when acquiring such effectiveness is a metal wire with a diameter of 1-10mm, and its outer diameter of said component formed in the pattern of an abbreviation swirl, the shape of an approximately concentric circle, and the letter of an abbreviation cuff is smaller than the bore of said container about 5mm, and it is desirable that the pitch of a pattern is 5-15mm. In the case of the conditions which separated from these values, mixing [of said conductive fine particles] is easy to become inadequate, and the deposit efficiency of said catalyst ingredient tends to fall.

[0081] Moreover, since it is the same as that of the case where the above-mentioned ball is used, it is desirable that the thickness of said component formed so that it might be an abbreviation plane as said oscillating magnification means and the pattern of an abbreviation swirl, the shape of an approximately concentric circle, and the letter of an abbreviation cuff might be made to the thickness which said conductive fine particles make is 10 - 70%.

[0082] As for the electric resistance of the conductive fine particles 1, it is desirable that they are 10 to 3 or less ohm-m, and it is desirable to use at least one of carbon and ITO (Indium tin oxide: conductive oxide which doped tin to the indium oxide), and SnO₂ sorts.

[0083] When using carbon as conductive fine particles 1, and it is desirable to carry out specific surface area of this carbon to more than 300m²/g and it is under 300m²/g, the property as a conductive catalyst particle may fall.

[0084] Moreover, when the 1st [based on this invention] or 2nd gaseous diffusion nature catalyst electrode is produced using the 1st [based on this invention], or 2nd conductive catalyst particle and carbon is used as conductive fine particles 1 although gas permeability serves as important engine performance, good gas permeability can be acquired by setting oil absorption of this carbon to 200ml / 100g or more.

[0085] Although it can form a catalyst bed by press working of sheet metal etc. also in itself, if membranes are bound and formed with resin, since the 1st [based on this invention] or 2nd conductive catalyst particle can hold said conductive catalyst fine particles by reinforcement sufficient on a porous gaseous diffusion nature charge collector, it is more desirable on manufacture of the 1st [based on this invention], or 2nd gaseous diffusion nature catalyst electrode.

[0086] The 1st [based on this invention] or 2nd gaseous diffusion nature catalyst electrode may contain other components, such as resin for consisting only of the 1st [based on this invention], or 2nd conductive catalyst particle, or binding this particle other than the 1st [based on this invention], or 2nd conductive catalyst particle substantially, as mentioned above. In the case of the latter, as said other

components, it is good to use water-repellent resin (for example, fluorine system) in respect of gas permeability, and to use an ion conductor etc. in respect of a binding property and wastewater nature, in respect of migratory [, such as an ostomy agent (for example, CaCO₃) and a proton,]. Furthermore, it is desirable to make the 1st [based on this invention] or 2nd conductive catalyst particle hold on a porous gaseous diffusion nature charge collector (for example, carbon sheet).

[0087] The 1st [based on this invention] or 2nd gaseous diffusion nature catalyst electrode is applicable to the electrochemistry device constituted as a fuel cell or a hydrogen manufacturing installation.

[0088] For example, in the fundamental structure which consists of the 1st pole, the 2nd pole, and an ion conductor pinched among these two poles, the 1st [based on this invention] or 2nd gaseous diffusion nature catalyst electrode is applicable to said 1st pole at least among said 1st pole and the 2nd pole.

[0089] Speaking still more concretely, it being possible for either [at least] the 1st pole or the 2nd pole to apply preferably the 1st [based on this invention] or 2nd gaseous diffusion nature catalyst electrode's to the electrochemistry device which is a gas electrode's.

[0090] Drawing 10 shows the fuel cell of an example using the 1st [based on this invention] gaseous diffusion nature catalyst electrode. The catalyst bed 18 in drawing 10 here on the front face of conductive fine particles (for example, carbon fine particles) Depending on the case besides the 1st [based on this invention to which said catalyst ingredient which consists of an alloy of said noble-metals ingredient (for example, Pt) and said charge of add-in material (for example, B) has adhered] conductive catalyst particle Are the mixolimnion which consists of mixture with an ion conductor, water-repellent resin (for example, fluorine system), and an ostomy agent (CaCO₃), and the 1st [based on this invention] gaseous diffusion nature catalyst electrode It is the porous gaseous diffusion nature catalyst electrode which consists of a catalyst bed 18 and a carbon sheet 19 as a porous gaseous diffusion nature charge collector. However, in a narrow sense, only a catalyst bed 18 may be called a gaseous diffusion nature catalyst electrode. Moreover, the ionic conduction section 20 is fastened between the 1st pole using the 1st [based on this invention] gaseous diffusion nature catalyst electrode, and the 2nd pole.

[0091] This fuel cell has the positive electrode (oxygen pole) 24 using the 1st [based on this invention the negative electrode (a fuel electrode or hydrogen pole) 22 using the 1st / based on this invention with terminal 21 / gaseous diffusion nature catalyst electrode which counters mutually, and with terminal 23] gaseous diffusion nature catalyst electrode (however, it is not necessary to necessarily use this for a positive electrode), and the ionic conduction section 20 is fastened among these two poles. At the time of use, it lets hydrogen pass all over H₂ passage 25 by the negative-electrode 22 side. While a fuel (H₂) passes through passage 25, a hydrogen ion is generated, this hydrogen ion moves to a positive-electrode 24 side with the hydrogen ion generated in the hydrogen ion generated with the negative electrode 22, and the ionic conduction section 20, it reacts with the oxygen (air) which passes along O₂ passage 26 there, and, thereby, desired electromotive force is taken out.

[0092] Since it is hard to generate sintering and this fuel cell has the good catalysis, since the 1st [based on this invention] gaseous diffusion nature catalyst electrode constitutes said 1st pole and 2nd pole, and the touch area of said catalyst ingredient and gas (H₂) is fully secured, the specific surface area of said catalyst ingredient contributed to a reaction becomes large, catalyst ability also improves, and good output characteristics are obtained. Moreover, since the hydrogen ion supplied from a negative-electrode 22 side moves to a positive-electrode 24 side, a hydrogen ion dissociating in a negative electrode 22, and a hydrogen ion dissociating in the ionic conduction section 20, there is the description that the conductivity of a hydrogen ion is high.

[0093] The hydrogen manufacturing installation of an example using the 1st [based on this invention] gaseous diffusion nature catalyst electrode is shown in the 1st pole of the above, and said 2nd pole at drawing 11 .

[0094] Here, the reaction in each electrode is shown below.

positive-electrode: -- H₂O->2H++1/2O₂+2e-negative-electrode: -- 2H++2e-->H₂** -- a required theoretical electrical potential difference becomes more than 1.23V.

[0095] Catalyst bed 18' in drawing 11 on the front face of said conductive fine particles (for example,

carbon fine particles) Depending on the case besides the 1st [based on this invention to which said catalyst ingredient which consists of an alloy of said noble-metals ingredient (for example, Pt) and said charge of add-in material (for example, B) has adhered in the shape of film] conductive catalyst particle Are the mixolimnion which consists of mixture with an ion conductor, water-repellent resin (for example, fluorine system), and an ostomy agent (CaCO₃ grade), and the 1st [based on this invention] gaseous diffusion nature catalyst electrode It is the porous gaseous diffusion nature catalyst electrode which consists of catalyst bed 18' and carbon-sheet 19' as a porous gaseous diffusion nature charge collector. Moreover, ionic conduction section 20' is fastened between the 1st pole using the 1st [based on this invention] gaseous diffusion nature catalyst electrode, and the 2nd pole.

[0096] at the time of use, a steam or steam content atmospheric air supplies this hydrogen manufacturing installation by the positive-electrode 24' side -- having -- this steam or steam content atmospheric air -- positive-electrode 24' -- it decomposes in a side -- having -- an electron and a proton (hydrogen ion) -- generating -- this electron and proton that were generated -- negative-electrode 22' -- a side -- moving -- this negative-electrode 22' -- it converts to hydrogen gas in a side, and, thereby, desired hydrogen gas is generated.

[0097] The proton and electron which need this hydrogen manufacturing installation for generation of the hydrogen in negative-electrode 22' which sintering could not generate easily and it described above since the 1st [based on this invention] gaseous diffusion nature catalyst electrode constituted said 1st pole at least among said 1st pole and the 2nd pole can move smoothly in the inside of an electrode.

[0098] the inside of the 1st [based on this invention], or 2nd gaseous diffusion nature catalyst electrode -- or as said usable ion conductor, fullerene derivatives other than general Nafion (Du Pont perfluoro sulfonic acid type resin), such as FURARE Norian (the Pori hydroxylation fullerene), are mentioned to said ionic conduction section pinched among the two poles of said 1st pole which constitutes said electrochemistry device, and the 2nd pole.

[0099] As shown in drawing 12 , as for FURARE Norian (Fullerenol) which has the structure which added two or more hydroxyl groups in a fullerene molecule, the synthetic example was first reported by Chiang and others in 1992 (1992 Chiang, L.Y.; Swirczewski, J.W.; Hsu, C.S.; Chowdhury, S.K.; Cameron, S.; Creegan, K., J.Chem. Soc, Chem.Commun. 1791).

[0100] As these people do outline illustration of such FURARE Norian at drawing 13 R> 3 (A), they consider as floc. The FURARE Norian molecule which approached each other (O shows a fullerene molecule among drawing.) When it was made for an interaction to arise in hydroxyl groups, the knowledge of this floc demonstrating a proton conduction property (if it putting in another way dissociative [of H⁺ from the phenolic hydroxyl group of a FURARE Norian molecule]) high as the macroscopic aggregate was able to be carried out for the first time.

[0101] Moreover, the floc of the fullerene which has two or more OSO₃H sets in addition to above-mentioned FURARE Norian can also be used as said ion conductor. The Pori hydroxylation fullerene, i.e., sulfuric-acid hydrogen esterification FURARE Norian, as shown in drawing 13 (B) to which the OH radical replaced the OSO₃H set is too reported by Chiang and others in 1994 (59 Chiang, L.Y.; Wang, L.Y.; Swirczewski, J.W.; Soled, S.; Cameron, S., J.Org.Chem.1994, 3960). There are some which contain only OSO₃H set in one intramolecular in the fullerene by which sulfuric-acid hydrogen esterification was carried out, or plurality and giving are also possible respectively in this radical and hydroxyl group.

[0102] When much FURARE Norians mentioned above and sulfuric-acid hydrogen esterification FURARE Norians are made to condense, the proton conductivity which it shows as bulk In order to concern with migration directly the proton originating in a lot of hydroxyl groups contained in intramolecular from the first, or OSO₃H sets, It is not necessary to incorporate the hydrogen and the proton which make a steam molecule etc. the origin from an ambient atmosphere and, and there are not supply of the moisture from the outside and constraint of as opposed to [it is not necessary to especially absorb moisture etc. from the open air, and] an ambient atmosphere. Therefore, it can be continuously used for the bottom of a desiccation ambient atmosphere.

[0103] Moreover, especially, the fullerene used as the base of these molecules has an electrophilic

property, is considered that this has contributed to promotion of ionization of a hydrogen ion greatly also not only in OSO₃H set with high acidity but in a hydroxyl group etc., and shows the outstanding proton conductivity. Moreover, since quite many hydroxyl groups, OSO₃H set, etc. can be introduced into one fullerene molecule and the number density per unit volume of a conductor of the proton which participates in conduction increases very much, effectual conductivity is discovered.

[0104] Since the most consists of carbon atoms of fullerene, above-mentioned FURARE Norian and sulfuric-acid hydrogen esterification FURARE Norian have light weight, and cannot carry out deterioration easily, either, and a pollutant is not contained, either. The manufacturing cost of fullerene is also falling rapidly. the environment like a resource ---like -- economical -- seeing -- which ingredient of others [fullerene] -- furthermore, it is thought that it is a carbon system ingredient near an ideal.

[0105] Furthermore, what has -COOH, -SO₃H, or -OPO(OH)₂ in a fullerene molecule in addition to for example, the above-mentioned -OH and -OSO₃H is usable.

[0106] In order to compound above-mentioned FURARE Norian etc., as opposed to the powder of a fullerene molecule, a desired radical can be introduced into the configuration carbon atom of a fullerene molecule by giving combining well-known processing of acid treatment, hydrolysis, etc. suitably.

[0107] Here, as said ion conductor which constitutes the above-mentioned ionic conduction section, when the above-mentioned fullerene derivative is used, it is desirable for this ion conductor to consist only of a fullerene derivative substantially, or to be bound with the binder.

[0108] In addition, the fullerene derivative currently bound with the binder may be used for the ionic conduction section 17 and 17' instead of the ion conductor pinched by the 1st pole of the above which consists only of the above-mentioned fullerene derivative of the shape of film acquired by carrying out pressing of the above-mentioned fullerene derivative, and the 2nd pole. In this case, ionic conduction section with sufficient reinforcement can be formed by being bound with a binder.

[0109] Here, one sort of the polymer which has well-known membrane formation nature as polymeric materials usable as the above-mentioned binder, or two sorts or more are used, and the loadings in the ionic conduction section are usually stopped to 20 or less % of the weight. It is because there is a possibility of reducing the conductivity of a hydrogen ion when it exceeds 20 % of the weight.

[0110] Since such the ionic conduction section of a configuration also contains the above-mentioned fullerene derivative as an ion conductor, it can demonstrate the same hydrogen ion conductivity as the above-mentioned ion conductor which consists only of a fullerene derivative substantially.

[0111] And the membrane formation nature which originates in polymeric materials unlike a fullerene derivative independent case is given, and compared with the powder compression-molding article of a fullerene derivative, reinforcement is large and it can use as a flexible ion conductivity thin film (thickness is usually 300 micrometers or less) which has gas transparency prevention ability.

[0112] In addition, especially limitation is not carried out, if the conductivity of a hydrogen ion is not checked as much as possible (based on a reaction with a fullerene derivative) but it has membrane formation nature as the above-mentioned polymeric materials. Usually, it does not have electronic conduction nature but what has good stability is used. When the example is given, there are poly fluoro ethylene, polyvinylidene fluoride, polyvinyl alcohol, etc., and these are desirable polymeric materials also from the reason explained below.

[0113] First, the thing with desirable poly fluoro ethylene is because a bigger thin film than that strong can be easily formed with little loadings compared with other polymeric materials. The loadings in this case are preferably as little as 0.5 - 1.5 % of the weight 3 or less % of the weight, and end, and thickness of a thin film is usually thinly made with from 100 micrometers to 1 micrometer.

[0114] Moreover, the thing with desirable polyvinylidene fluoride and polyvinyl alcohol is because the ion conductivity thin film which has the more excellent gas transparency prevention ability is obtained. The loadings in this case are good to consider as 5 - 15% of the weight of the range.

[0115] poly fluoro ethylene -- an imitation -- polyvinylidene fluoride and polyvinyl alcohol -- an imitation -- when less than the lower limit of each range which those loadings mentioned above, it may have a bad influence on membrane formation

[0116] What is necessary is to begin pressing and extrusion molding and just to use the well-known

forming-membranes method, in order to obtain the thin film of the ionic conduction section to which it comes to bind each fullerene derivative of the gestalt of this operation with a binder.

[0117]

[Example] Hereafter, based on an example, this invention is explained concretely. In addition, an example 1 - an example 5 explain the 1st invention based on this invention concretely, and an example 6 - an example 12 explain the 2nd invention based on this invention concretely.

[0118] Using the equipment shown in example 1 drawing 1 (A), the spatter target, the trembler, and the container have been arranged and conductive fine particles and a ball have been arranged in said container. What was introduced so that it might become each addition which shows B in the following table 1 after a spatter to Pt with a particle size [as shown in drawing 1 (B)] of 100mm was used for said spatter target. Said conductive fine particles used surface area 800m²/g, the oil absorption of 360ml / 100g carbon fine particles for the ball of the product [ball / said] made from the stainless steel of 3mm of diameters. And the spatter was performed, generating **1mm of vibration, and vibration with a vibration frequency of 36Hz using said vibrator.

[0119] Ball 35g of 1g of carbon fine particles and the product made from stainless steel is supplied in the basis of the above-mentioned conditions, and a container. Gas introducing Ar (1Pa), impressing RF of 400W to a target, and adding vibration with vibrator to carbon fine particles and a ball When the spatter was performed for 30 minutes, carbon fine particles were increasing to the weight of 1.66g, and said catalyst ingredient which consists of an alloy of 0.66g Pt/B adhered on carbon. This is equivalent to the weight ratio of 40wt%Pt support carbon.

[0120] Subsequently, on the carbon sheet, the binder which consists of Teflon (trademark), and the solvent which comes to knead carbon (what has not adhered platinum) were applied so that it might be set to 20 micrometers after desiccation, it sank in and this was made into the prevention layer.

[0121] Moreover, each carbon fine particles which were obtained by the above-mentioned approach and which supported the Pt/B alloy were kneaded with nPA (normal propyl alcohol) as the perfluoro sulfonic acid and organic solvent as a binder, spreading desiccation of this mixed liquor was carried out so that spreading formation might be carried out, it might sink in on a carbon sheet and the coating thickness after desiccation might be set to 10 micrometers on a prevention layer, and each gaseous diffusion nature catalyst electrode was obtained. These gaseous diffusion nature catalyst electrodes have been arranged to both-sides side of ion exchange membrane (perfluoro sulfonic acid), the fuel cell as shown in drawing 10 was produced, and the initial output and the output after 200-hour operation were measured. The result of the output measurement of each fuel cell using each gaseous diffusion nature catalyst electrode with which B additions differ, respectively is combined with the following table 1 and drawing 14 , and is shown. In addition, the initial output (unit mW/cm²) of the fuel cell using the gaseous diffusion nature catalyst electrode which did not add B was made into 100% by the relative value, and this was made into the reference value.

[0122]

[Table 1]

表1

| 添加元素 | 添加量(at%) | 初期出力(%) | 200時間運転後出力 |
|------|----------|---------|------------|
| B | 0 | 100 | 75 |
| B | 1 | 100 | 80 |
| B | 1.5 | 100 | 82 |
| B | 2.0 | 105 | 95 |
| B | 2.5 | 107 | 107 |
| B | 3 | 108 | 108 |
| B | 5 | 110 | 110 |
| B | 10 | 115 | 115 |
| B | 20 | 120 | 120 |
| B | 30 | 130 | 130 |
| B | 40 | 130 | 130 |
| B | 50 | 130 | 130 |
| B | 60 | 120 | 120 |
| B | 65 | 115 | 115 |
| B | 70 | 110 | 110 |
| B | 75 | 95 | 95 |
| B | 80 | 80 | 80 |

[0123] As mentioned above, B as Pt and said charge of add-in material as said noble-metals ingredient is a non-dissolving system, and was able to be alloyed with said physical vapor deposition, such as a spatter, to the ability not to alloy with heating of the chemical technique so that clearly. Moreover, the 1st [based on this invention] gaseous diffusion nature catalyst electrode Since the 1st [based on this invention which comes to adhere to the front face of said conductive fine particles by the spatter in said catalyst ingredient which consists of an alloy of Pt as said noble-metals ingredient and B as said charge of add-in material] conductive catalyst particle is contained The internal self-diffusion of Pt crystal lattice in said catalyst ingredient is prevented, and it is hard to generate sintering, has the outstanding catalytic activity as compared with the case of only Pt, and excelled in output characteristics.

[0124] Moreover, since said catalyst ingredient was made to adhere to the front face of said carbon fine particles, arranging the carbon fine particles as said conductive fine particles, and the ball as said oscillating magnification means on said plane of vibration, and vibrating these, said carbon fine particles vibrated more and stopping of them at one on said plane of vibration was lost. Therefore, said catalyst ingredient was able to be made to adhere to homogeneity to said whole carbon fine particles arranged in said container.

[0125] Furthermore, by making the addition of B as said charge of add-in material into 2-70-mol% or at % and the specific range, the more effective sintering prevention effectiveness is acquired, and it can have better catalytic activity, and it became possible to maintain a high output over a long time so that more clearly than Table 1 and drawing 14 .

[0126] an example 2 -- B as said charge of add-in material -- instead of -- SiO₂ -- using -- and the fuel cell as shown in drawing 10 was produced like the example 1, respectively except having changed the addition of SiO₂, as shown in the following table 2. The result of having measured the initial output of each fuel cell and the output after 200-hour operation is combined with the following table 2 and drawing 15 , and is shown. In addition, the initial output (unit mW/cm²) of the fuel cell using the gaseous diffusion nature catalyst electrode which did not add SiO₂ was made into 100% by the relative value, and this was made into the reference value.

[0127]

[Table 2]

表2

| 添加元素 | 添加量(mol%) | 初期出力(%) | 200時間運転後出力 |
|------------------|-----------|---------|------------|
| SiO ₂ | 0 | 100 | 75 |
| SiO ₂ | 1 | 100 | 82 |
| SiO ₂ | 1.5 | 100 | 85 |
| SiO ₂ | 2.0 | 107 | 100 |
| SiO ₂ | 2.5 | 109 | 107 |
| SiO ₂ | 3 | 110 | 108 |
| SiO ₂ | 5 | 110 | 110 |
| SiO ₂ | 10 | 115 | 115 |
| SiO ₂ | 20 | 120 | 120 |
| SiO ₂ | 30 | 130 | 130 |
| SiO ₂ | 40 | 130 | 130 |
| SiO ₂ | 50 | 130 | 130 |
| SiO ₂ | 60 | 120 | 120 |
| SiO ₂ | 65 | 115 | 115 |
| SiO ₂ | 70 | 110 | 110 |
| SiO ₂ | 75 | 95 | 95 |
| SiO ₂ | 80 | 80 | 80 |

[0128] As mentioned above, Pt as said noble-metals ingredient and SiO₂ as said charge of add-in material are non-dissolving systems, and were able to be alloyed only with said physical vapor deposition, such as a spatter, to the ability not to alloy with heating of the chemical technique so that clearly. Moreover, the 1st [based on this invention] gaseous diffusion nature catalyst electrode Since the 1st [based on this invention which comes to adhere to the front face of said conductive fine particles by the spatter in said catalyst ingredient which consists of an alloy of Pt as said noble-metals ingredient and SiO₂ as said charge of add-in material] conductive catalyst particle is contained The internal self-diffusion of Pt crystal lattice in said catalyst ingredient is prevented, and it is hard to generate sintering, has the outstanding catalytic activity as compared with the case of only Pt, and excelled in output characteristics.

[0129] Moreover, since said catalyst ingredient was made to adhere to the front face of said carbon fine particles, arranging the carbon fine particles as said conductive fine particles, and the ball as said oscillating magnification means on said plane of vibration, and vibrating these, said carbon fine particles vibrated more and stopping of them at one on said plane of vibration was lost. Therefore, said catalyst ingredient was able to be made to adhere to homogeneity to said whole carbon fine particles arranged in said container.

[0130] By making the addition of SiO₂ as said charge of add-in material into 2-70-mol% or at % and the specific range, the more effective sintering prevention effectiveness is acquired, and it can have better catalytic activity, and it became possible to maintain a high output over a long time so that more clearly than Table 2 and drawing 15 .

[0131] Moreover, even if it used SiO instead of SiO₂ as said charge of add-in material, the completely same effectiveness as the case where SiO₂ is used was observed. Moreover, also when a part of SiO₂ was replaced by B, the same effectiveness was completely acquired.

[0132] an example 3 -- B as said charge of add-in material -- instead of -- Ga₂O -- the fuel cell as shown in drawing 10 was produced like the example 1, respectively except having changed the addition of Ga₂O₃, as shown in the following table 3, using 3. The result of having measured the initial output of each fuel cell and the output after 200-hour operation is combined with the following table 3 and drawing 16 , and is shown. In addition, the initial output (unit mW/cm²) of the fuel cell using the gaseous diffusion nature catalyst electrode which did not add Ga₂O₃ was made into 100% by the relative value, and this was made into the reference value.

[0133]

[Table 3]

表3

| 添加元素 | 添加量(mol%) | 初期出力(%) | 200時間運転後出力 |
|--------------------------------|-----------|---------|------------|
| Ga ₂ O ₃ | 0 | 100 | 75 |
| Ga ₂ O ₃ | 1 | 100 | 82 |
| Ga ₂ O ₃ | 1.5 | 100 | 85 |
| Ga ₂ O ₃ | 2.0 | 102 | 95 |
| Ga ₂ O ₃ | 2.5 | 106 | 98 |
| Ga ₂ O ₃ | 3 | 110 | 108 |
| Ga ₂ O ₃ | 5 | 110 | 110 |
| Ga ₂ O ₃ | 10 | 110 | 110 |
| Ga ₂ O ₃ | 20 | 110 | 110 |
| Ga ₂ O ₃ | 30 | 110 | 110 |
| Ga ₂ O ₃ | 40 | 110 | 110 |
| Ga ₂ O ₃ | 50 | 110 | 110 |
| Ga ₂ O ₃ | 60 | 110 | 110 |
| Ga ₂ O ₃ | 65 | 110 | 110 |
| Ga ₂ O ₃ | 70 | 110 | 110 |
| Ga ₂ O ₃ | 75 | 95 | 95 |
| Ga ₂ O ₃ | 80 | 80 | 80 |

[0134] an example 4 -- B as said charge of add-in material -- instead of -- V -- the fuel cell as shown in drawing 10 was produced like the example 1, respectively except having changed the addition of V₂O₅, as shown in the following table 4, using 2O5. The result of having measured the initial output of each fuel cell and the output after 200-hour operation is combined with the following table 4 and drawing 17, and is shown. In addition, the initial output (unit mW/cm²) of the fuel cell using the gaseous diffusion nature catalyst electrode which did not add V₂O₅ was made into 100% by the relative value, and this was made into the reference value.

[0135]

[Table 4]

表4

| 添加元素 | 添加量(mol%) | 初期出力(%) | 200時間運転後出力 |
|-------------------------------|-----------|---------|------------|
| V ₂ O ₅ | 1 | 100 | 82 |
| V ₂ O ₅ | 1.5 | 100 | 85 |
| V ₂ O ₅ | 2.0 | 100 | 95 |
| V ₂ O ₅ | 2.5 | 100 | 98 |
| V ₂ O ₅ | 3 | 100 | 100 |
| V ₂ O ₅ | 5 | 100 | 100 |
| V ₂ O ₅ | 10 | 100 | 100 |
| V ₂ O ₅ | 20 | 100 | 100 |
| V ₂ O ₅ | 30 | 100 | 100 |
| V ₂ O ₅ | 40 | 100 | 100 |
| V ₂ O ₅ | 50 | 100 | 100 |
| V ₂ O ₅ | 60 | 100 | 100 |
| V ₂ O ₅ | 65 | 100 | 100 |
| V ₂ O ₅ | 70 | 100 | 100 |
| V ₂ O ₅ | 75 | 95 | 95 |
| V ₂ O ₅ | 80 | 80 | 80 |

[0136] an example 5 -- B as said charge of add-in material -- instead of -- WO₃ -- using -- and the fuel cell as shown in drawing 10 was produced like the example 1, respectively except having changed the addition of WO₃, as shown in the following table 5. The result of having measured the initial output of each fuel cell and the output after 200-hour operation is combined with the following table 5 and drawing 18, and is shown. In addition, the initial output (unit mW/cm²) of the fuel cell using the gaseous diffusion nature catalyst electrode which did not add WO₃ was made into 100% by the relative value, and this was made into the reference value.

[0137]

[Table 5]

表5

| 添加元素 | 添加量(mol%) | 初期出力(%) | 200時間運転後出力 |
|-----------------|-----------|---------|------------|
| WO ₃ | 0 | 100 | 75 |
| WO ₃ | 1 | 100 | 82 |
| WO ₃ | 1.5 | 100 | 85 |
| WO ₃ | 2.0 | 107 | 100 |
| WO ₃ | 2.5 | 109 | 107 |
| WO ₃ | 3 | 110 | 108 |
| WO ₃ | 5 | 110 | 110 |
| WO ₃ | 10 | 115 | 115 |
| WO ₃ | 20 | 120 | 120 |
| WO ₃ | 30 | 130 | 130 |
| WO ₃ | 40 | 120 | 120 |
| WO ₃ | 50 | 115 | 115 |
| WO ₃ | 60 | 110 | 110 |
| WO ₃ | 65 | 110 | 110 |
| WO ₃ | 70 | 110 | 110 |
| WO ₃ | 75 | 95 | 95 |
| WO ₃ | 80 | 80 | 80 |

[0138] As mentioned above, Pt as said noble-metals ingredient, Ga 2O₃ as said charge of add-in material, V₂O₅, or WO₃ is a non-dissolving system, and was able to be alloyed only with said physical vapor deposition, such as a spatter, to the ability not to alloy with heating of the chemical technique so that clearly. Moreover, the 1st [based on this invention] gaseous diffusion nature catalyst electrode Since the 1st [based on this invention which comes to adhere to the front face of said conductive fine particles by the spatter in said catalyst ingredient which consists of an alloy with Ga 2O₃ as Pt and said charge of add-in material as said noble-metals ingredient, V₂O₅, or WO₃] conductive catalyst particle is contained The internal self-diffusion of Pt crystal lattice in said catalyst ingredient is prevented, and it is hard to generate sintering, has the outstanding catalytic activity as compared with the case of only Pt, and excelled in output characteristics.

[0139] Moreover, since said catalyst ingredient was made to adhere to the front face of said carbon fine particles, arranging the carbon fine particles as said conductive fine particles, and the ball as said oscillating magnification means on said plane of vibration, and vibrating these, said carbon fine particles vibrated more and stopping of them at one on said plane of vibration was lost. Therefore, said catalyst ingredient was able to be made to adhere to homogeneity to said whole carbon fine particles arranged in said container.

[0140] By making the addition of Ga 2O₃ as said charge of add-in material, V₂O₅, or WO₃ into 2-70-mol% or at % and the specific range, the more effective sintering prevention effectiveness is acquired, and it can have better catalytic activity, and it became possible to maintain a high output over a long time so that more clearly than Tables 3 and 4 or 5 and drawing 16, 17, or 18.

[0141] Using the equipment shown in example 6 drawing 3 (A), the spatter target, the trembler, and the container have been arranged and the ball as conductive fine particles and said oscillating magnification means has been arranged in said container. said each alloying element as MII shown in the following table 6 to Pt with a particle size [as said MI as shows said spatter target to drawing 3 (B)] of 100mm -- 3at(s)% -- what was introduced was used. Said conductive fine particles used surface area 800m²/g, the oil absorption of 360ml / 100g carbon fine particles for the ball of the product [ball / said] made from the stainless steel of 3mm of diameters. And the spatter was performed, generating **1mm of vibration, and vibration with a vibration frequency of 36Hz using said vibrator.

[0142] Ball 35g of 1g of carbon fine particles and the product made from stainless steel is supplied in the basis of the above-mentioned conditions, and a container. Gas introducing Ar (1Pa), impressing RF of 400W to a target, and adding vibration with vibrator to carbon fine particles and a ball When the spatter was performed for 30 minutes, carbon fine particles were increasing to the weight of 1.66g, and said catalyst ingredient which consists of an alloy of 0.66g Pt / each alloying element (said MII) adhered on carbon. This is equivalent to the weight ratio of 40wt%Pt support carbon.

[0143] Subsequently, on the carbon sheet, the binder which consists of Teflon (trademark), and the solvent which comes to knead carbon (what has not adhered platinum) were applied so that it might be set to 20 micrometers after desiccation, it sank in and this was made into the prevention layer.

[0144] moreover, each carbon fine particles which were obtained by the above-mentioned approach and which supported Pt / alloying element (said MII) alloy were kneaded with nPA (normal propyl alcohol) as the perfluoro sulfonic acid and organic solvent as a binder, and spreading formation of this mixed liquor was carried out on the carbon sheet -- spreading desiccation was carried out so that it might sink in and the coating thickness after desiccation might be set to 20 micrometers on a prevention layer, and each gaseous diffusion nature catalyst electrode was obtained. These gaseous diffusion nature catalyst electrodes have been arranged to both-sides side of ion exchange membrane (perfluoro sulfonic acid), the fuel cell as shown in drawing 10 was produced, and the initial output and the output after 200-hour operation were measured. The measurement result is collectively shown in the following table 6. In addition, the initial output (unit mW/cm²) of the fuel cell using the gaseous diffusion nature catalyst electrode which did not add said alloying element as MII was made into 100% by the relative value, and this was made into the reference value.

[0145] an example 7 -- said each alloying element as MII shown in the following table 7 as a target like an example 6 to Pt with a particle size [as shown in drawing 3 (B) / as said MI] of 100mm except having not used the ball as said oscillating magnification means -- 3at(s)% -- the spatter was performed using what was introduced and each gaseous diffusion nature catalyst electrode was produced. These gaseous diffusion nature catalyst electrodes have been arranged to both-sides side of ion exchange membrane, the fuel cell as shown in drawing 10 was produced, and the initial output and the output after 200-hour operation were measured. The measurement result is collectively shown in the following table 7. In addition, the initial output (unit mW/cm²) of the fuel cell using the gaseous diffusion nature catalyst electrode in an example 6 which did not add said alloying element as MII was made into 100% by the relative value, and this was made into the reference value.

[0146] Except having not made it vibrate, not using the ball as an example 8 aforementioned oscillating magnification means said each alloying element as MII shown in the following table 8 as a target like an example 6 to Pt with a particle size [as shown in drawing 3 (B) / as said MI] of 100mm -- 3at(s)% -- the spatter was performed using what was introduced and each gaseous diffusion nature catalyst electrode was produced. These gaseous diffusion nature catalyst electrodes have been arranged to both-sides side of ion exchange membrane, the fuel cell as shown in drawing 10 was produced, and the initial output and the output after 200-hour operation were measured. The measurement result is collectively shown in the following table 8. In addition, the initial output (unit mW/cm²) of the fuel cell using the gaseous diffusion nature catalyst electrode in an example 1 which did not add said alloying element as MII was made into 100% by the relative value, and this was made into the reference value.

[0147]

[Table 6]

表6 (ボール有り+振動有り)

| | 添加元素 | 添加量(at%) | 初期出力(%) | 200時間運転後出力(%) |
|------|------|----------|---------|---------------|
| - | 無し | 0 | 100 | 75 |
| MII' | Fe | 3 | 100 | 100 |
| | Co | 3 | 100 | 100 |
| | Ni | 3 | 100 | 100 |
| | Cr | 3 | 100 | 100 |
| | Al | 3 | 100 | 100 |
| | Hf | 3 | 100 | 100 |

[Table 7]

表7 (ボールなし+振動有り)

| | 添加元素 | 添加量(at%) | 初期出力(%) | 200時間運転後出力(%) |
|-------|------|----------|---------|---------------|
| 実施例1 | 無し | 0 | 100 | 75 |
| | Fe | 3 | 60 | 60 |
| | Co | 3 | 60 | 60 |
| MII' | Ni | 3 | 60 | 60 |
| | Cr | 3 | 60 | 60 |
| | Al | 3 | 60 | 60 |
| MII'' | Hf | 3 | 60 | 60 |

[Table 8]

表8 (ボールなし+振動なし)

| | 添加元素 | 添加量(at%) | 初期出力(%) | 200時間運転後出力(%) |
|-------|------|----------|---------|---------------|
| 実施例1 | 無し | 0 | 100 | 75 |
| | Fe | 3 | 30 | 30 |
| | Co | 3 | 30 | 30 |
| MII' | Ni | 3 | 30 | 30 |
| | Cr | 3 | 30 | 30 |
| | Al | 3 | 30 | 30 |
| MII'' | Hf | 3 | 30 | 30 |

[0148] As mentioned above, Pt as said MI and said each alloying element as MII were able to be alloyed with said physical vapor deposition, such as a spatter, so that clearly. Moreover, the 2nd [based on this invention] gaseous diffusion nature catalyst electrode Since the 2nd [based on this invention which comes to adhere to the front face of said conductive fine particles by the spatter in said catalyst ingredient which consists of an alloy of Pt as said MI and each of said alloying element as MII] conductive catalyst particle is contained The internal self-diffusion of Pt crystal lattice in said catalyst ingredient was prevented, it was hard to generate sintering, and the output with a good rear spring supporter was able to be maintained more to the long time as compared with the case of only Pt.

[0149] Moreover, when making said catalyst ingredient adhere to the front face of said carbon fine particles, vibrating the carbon fine particles as said conductive fine particles, compared with the case where it is made to adhere without making it vibrate, said catalyst ingredient could be adhered more to homogeneity to said carbon fine particles, and the output improved more.

[0150] Furthermore, compared with the case where it is made to vibrate without the front face of said carbon fine particles adhering said catalyst ingredient, and adding ** and said ball, arranging the ball as the carbon fine particles and said oscillating magnification means as said conductive fine particles on said plane of vibration, and vibrating these, said carbon fine particles vibrated further and stopping of them at one on said plane of vibration was lost. Therefore, to said whole carbon fine particles arranged in said container, said catalyst ingredient could be made to adhere to homogeneity further, and the output improved further.

[0151] Said MII here besides each alloying element shown in Table 6, 7, and 8 Fe, Co, nickel, Cr, aluminum, Cu, Hf, Zr, Ti, V, Nb, Also when at least one sort chosen from Ta, W, Ga, Sn, germanium, Si, Re, Os, Pb, Bi, Sb, Mo, Mn, O, N, F, C, Zn, In, and rare earth elements was introduced, the same effectiveness was acquired with having mentioned above.

[0152] As shown in the example 9 following table 9, the fuel cell as shown in drawing 10 was produced like the example 6, respectively except having changed said class of alloying element and its addition as MII. The result of having measured the initial output of each fuel cell and the output after 200-hour operation is combined with the following table 9 and drawing 19, and is shown. In addition, the initial output (unit mW/cm²) of the fuel cell using the gaseous diffusion nature catalyst electrode which did not add said alloying element as MII was made into 100% by the relative value, and this was made into the reference value.

[0153]

[Table 9]

表9

| | 添加元素 | 添加量(at%) | 初期出力(%) | 200時間運転後出力(%) |
|------|------|----------|---------|---------------|
| — | 無し | 0 | 100 | 75 |
| MII' | Fe | 0.3 | 100 | 75 |
| | Fe | 0.4 | 100 | 76 |
| | Fe | 0.5 | 100 | 86 |
| | Fe | 0.6 | 100 | 89 |
| | Fe | 0.7 | 100 | 92 |
| | Co | 0.3 | 100 | 75 |
| | Co | 0.4 | 100 | 76 |
| | Co | 0.5 | 100 | 86 |
| | Co | 0.6 | 100 | 89 |
| | Co | 0.7 | 100 | 92 |
| MII' | Hf | 0.3 | 100 | 80 |
| | Hf | 0.4 | 100 | 76 |
| | Hf | 0.5 | 100 | 86 |
| | Hf | 0.6 | 100 | 89 |
| | Hf | 0.7 | 100 | 92 |

[0154] By specifying the addition of each of said alloying element as MII more than with 0.5at%, the more effective sintering prevention effectiveness is acquired, and it can have better catalytic activity, and it became possible to maintain a high output over a long time so that more clearly than Table 9 and drawing 19 . 0. In the case of below 5at%, since there were too few said amounts of MII, the sintering prevention effectiveness might decrease.

[0155] The fuel cell as shown in drawing 10 was produced like the example 6, respectively except having changed the addition of Fe, as shown in the following table 10 as the example 10 above MII, using Fe belonging to said MII'. The result of having measured the initial output of each fuel cell and the output after 200-hour operation is collectively shown in the following table 10 and drawing 2020 . In addition, the initial output (unit mW/cm²) of the fuel cell using the gaseous diffusion nature catalyst electrode which did not add Fe was made into 100% by the relative value, and this was made into the reference value.

[0156]

[Table 10]

表10

| 添加元素 | 添加量(at%) | 初期出力(%) | 200時間運転後出力(%) |
|------|----------|---------|---------------|
| 無し | 0 | 100 | 75 |
| Fe | 10 | 105 | 105 |
| Fe | 20 | 110 | 110 |
| Fe | 30 | 120 | 120 |
| Fe | 40 | 120 | 120 |
| Fe | 50 | 120 | 120 |
| Fe | 56 | 115 | 115 |
| Fe | 60 | 110 | 110 |
| Fe | 62 | 83 | 83 |
| Fe | 70 | 80 | 80 |

[0157] When Fe belonging to said MII' was used as said MII so that more clearly than Table 10 and drawing 20 , while much more outstanding sintering prevention effectiveness was acquired by specifying the addition with less than [60at%], much more good output was obtained. When 60at(s)% was exceeded, sintering was able to be prevented, but since there were too many additions of Fe, the output might decline.

[0158] Moreover, although the example 10 showed the example which uses Fe belonging to said MII' as said MII, the same result was obtained even if it used at least one sort chosen from Fe, Co, nickel, Cr, aluminum, Sn, Cu, Mo, W, O, N, F, and C.

[0159] The fuel cell as shown in drawing 10 was produced like the example 6, respectively except having changed the addition of Hf, as shown in the following table 11 as the example 11 above MII, using Hf belonging to said MII." The result of having measured the initial output of each fuel cell and the output after 200-hour operation is collectively shown in the following table 11 and drawing 2121 . In addition, the initial output (unit mW/cm²) of the fuel cell using the gaseous diffusion nature catalyst electrode which did not add Hf was made into 100% by the relative value, and this was made into the

reference value.

[0160]

[Table 11]

表11

| 添加元素 | 添加量(at%) | 初期出力(%) | 200時間運転後出力(%) |
|------|----------|---------|---------------|
| 無し | 0 | 100 | 75 |
| Hf | 5 | 100 | 100 |
| Hf | 10 | 95 | 95 |
| Hf | 15 | 90 | 90 |
| Hf | 18 | 88 | 88 |
| Hf | 20 | 85 | 85 |
| Hf | 22 | 76 | 76 |
| Hf | 25 | 70 | 70 |
| Hf | 30 | 60 | 60 |

[0161] The good output was obtained while much more outstanding sintering prevention effectiveness was acquired by specifying the addition with less than [20at%], when Hf belonging to said MII" was used as said MII so that more clearly than Table 11 and drawing 21 . When 20at(s)% was exceeded, sintering was able to be prevented, but since there were too many additions of Hf, the output might decline.

[0162] Moreover, although the example 11 showed the example which uses Hf belonging to said MII" as said MII, the same result was obtained even if it used at least one sort chosen from Hf, Zr, Ti, V, Nb, Ta, Ga, germanium, Si, Re, Os, Pb, Bi, Sb, Mn, and rare earth elements.

[0163] The fuel cell as shown in drawing 10 was produced like the example 6, respectively except having changed the addition of each alloying element, as shown in following following Table 12 and 13 as the example 12 above MII, using the mixture of Fe belonging to said MII', and Hf belonging to said MII." It reaches following table 12, and the result of having measured the initial output of each fuel cell and the output after 200-hour operation is combined with drawing 22 , the following table 13, and drawing 23 , and is shown. In addition, the initial output (unit mW/cm2) of the fuel cell using the gaseous diffusion nature catalyst electrode which did not add the mixture of Fe belonging to said MII' and Hf belonging to said MII" was made into 100% by the relative value, and this was made into the reference value.

[0164]

[Table 12]

表12 $b+c \geq 0.5$ に対して

| 添加元素とその添加量(at%) | 初期出力(%) | 200時間運転後出力(%) |
|-----------------------|---------|---------------|
| 無し | 100 | 75 |
| Hf(0.2at%)+Fe(0.2at%) | 100 | 76 |
| Hf(0.2at%)+Fe(0.3at%) | 100 | 86 |
| Hf(0.2at%)+Fe(0.4at%) | 100 | 89 |
| Hf(0.2at%)+Fe(0.5at%) | 100 | 92 |

[Table 13]

表13 $b+c \leq 60$ に対して

| 添加元素とその添加量(at%) | 初期出力(%) | 200時間運転後出力(%) |
|---------------------|---------|---------------|
| 無し | 100 | 75 |
| Hf(10at%)+Fe(10at%) | 110 | 110 |
| Hf(10at%)+Fe(20at%) | 120 | 120 |
| Hf(10at%)+Fe(30at%) | 120 | 120 |
| Hf(10at%)+Fe(40at%) | 120 | 120 |
| Hf(10at%)+Fe(46at%) | 115 | 115 |
| Hf(10at%)+Fe(50at%) | 110 | 110 |
| Hf(10at%)+Fe(52at%) | 83 | 83 |
| Hf(10at%)+Fe(60at%) | 80 | 80 |

[0165] As mentioned above, even if it uses the mixture which consists of Fe as said MII', and Hf as said MII" as said MII (Fea-Hfb) so that clearly By the outstanding sintering prevention effectiveness and the outstanding output equivalent to the case where each alloying element is used independently being obtained, and specifying said addition of MII with the range of $0.5at\% \leq b+c \leq 60at\%$ Since it has much more outstanding catalyst ability, and the output was able to improve more and generating of sintering

was prevented much more effectively, high power was more maintainable over the long time. When the value of said b+c was less than [0.5at%] so that more clearly than Table 12 and drawing 22 , since there were too few additions of said MII' and said MII" , the sintering prevention effectiveness might decrease. Moreover, when 60at% was exceeded so that more clearly than Table 13 and drawing 23 , since there are too many additions of said MII' and said MII" , a catalysis tended to fall, and the output might decline.

[0166] the example explained above can deform into versatility based on the technical thought of this invention.

[0167] For example, in an example 1 - an example 5, although Pt was used as said noble-metals ingredient, Ir, Rh, etc. are usable, and although said carbon fine particles were used as said conductive fine particles, said ITO and SnO₂ grade are also usable.

[0168] In an example 6 - an example 12 moreover, said MII' Not only the alloying element used in each above-mentioned example but Fe, Co, nickel, At least one sort chosen from Cr, aluminum, Sn, Cu, Mo, W, O, N, F, and C can be used. Said MII" At least one sort chosen not only from an alloying element but from ** Hf, Zr, Ti, V, Nb, Ta, Ga, germanium, Si, Re, Os, Pb, Bi, Sb, and Mn and rare earth elements which were used in each above-mentioned example can be used.

[0169] Moreover, at least one sort chosen from noble-metals elements, such as Ir, Pd, Rh, Au, and Ru, although Pt was used as said MI is usable, and although said carbon fine particles were used as said conductive fine particles, said ITO and SnO₂ grade are also usable.

[0170] Moreover, as said oscillating magnification means, although said ball was used, the components of the shape of an abbreviation swirl as shown in drawing 7 , the components of the shape of an approximately concentric circle as shown in drawing 8 R> 8 , and the components of the letter of an abbreviation cuff as shown in drawing 9 could be used, and the result with all equivalent to examples 1-12 of having excelled was obtained.

[0171] Furthermore, although said fuel cell using the 1st [based on this invention] or 2nd gaseous diffusion nature catalyst electrode was explained, said gaseous diffusion nature catalyst electrode is applicable also to said hydrogen manufacturing installation which is the reverse reaction of said fuel cell.

[0172]

[Function and Effect of the Invention] Since said charge of add-in material of a non-dissolving system is made to adhere to the front face of said conductive fine particles with said physical vapor deposition thermally to said noble-metals ingredient and said noble-metals ingredient at coincidence according to invention of the 1st of this invention Properly speaking, said charge of add-in material of a non-dissolving system which does not make an alloy with heating with said noble-metals ingredient, either It can introduce compulsorily into the crystal lattice of said noble-metals ingredient, and the conductive catalyst particle by which said catalyst ingredient which consists of an alloy of said noble-metals ingredient and said charge of add-in material comes to adhere to the front face of said conductive fine particles can be obtained. Since this conductive catalyst particle contains said charge of add-in material in said catalyst ingredient, the internal self-diffusion of the crystal lattice of said noble-metals ingredient in said catalyst ingredient is prevented, and **** sintering mentioned already cannot generate it easily. In addition, by the chemical adhesion approach by the conventional technique, said charge of add-in material of a non-dissolving system cannot be introduced into said noble-metals ingredient, and cannot obtain said alloy.

[0173] Moreover, since said charge of add-in material of a non-dissolving system is made to adhere to the front face of said conductive fine particles with said physical vapor deposition thermally to said noble-metals ingredient and said noble-metals ingredient at coincidence, growth of the particle size of said noble-metals ingredient at the time of adhesion is controlled, and it has the outstanding catalytic activity.

[0174] Furthermore, since said catalyst ingredient is made to adhere to the front face of said conductive fine particles with said physical vapor deposition At low temperature, the 1st conductive catalyst particle of this invention which can adhere to the front face of said conductive fine particles, and is obtained a

crystalline good catalyst ingredient Since a good catalysis can be obtained in said smaller amount of catalyst ingredients and the touch area of said catalyst ingredient and gas is fully secured, the specific surface area of said catalyst ingredient contributed to a reaction becomes large, and catalyst ability also improves.

[0175] According to invention of the 2nd of this invention, since said MI and said MII are made to adhere to the front face of said conductive fine particles with said physical vapor deposition at coincidence, said MII can be compulsorily introduced into the crystal lattice of said MI, and the conductive catalyst particle by which said catalyst ingredient which consists of said alloy of MI and said MII comes to adhere to the front face of said conductive fine particles can be obtained. Since this conductive catalyst particle contains said MII in said catalyst ingredient, the movement toward transition of said MI in said catalyst ingredient is checked, the internal self-diffusion of a crystal lattice is prevented, and it can prevent generating of **** sintering mentioned already.

[0176] Moreover, since said catalyst ingredient is made to adhere to the front face of said conductive fine particles with said physical vapor deposition At low temperature, the 2nd conductive catalyst particle of this invention which can adhere to the front face of said conductive fine particles, and is obtained a crystalline good catalyst ingredient Since a good catalysis can be obtained in said smaller amount of catalyst ingredients and the touch area of said catalyst ingredient and gas is fully secured, the specific surface area of said catalyst ingredient contributed to a reaction becomes large, and catalyst ability also improves.

[0177] According to the electrochemistry device with which the 1st gaseous diffusion nature electrode of this invention or the 2nd gaseous diffusion nature electrode constitutes at least one of said electrodes, generating of sintering can be prevented, good output characteristics are obtained, and these output characteristics can be maintained over a long time.

[Translation done.]

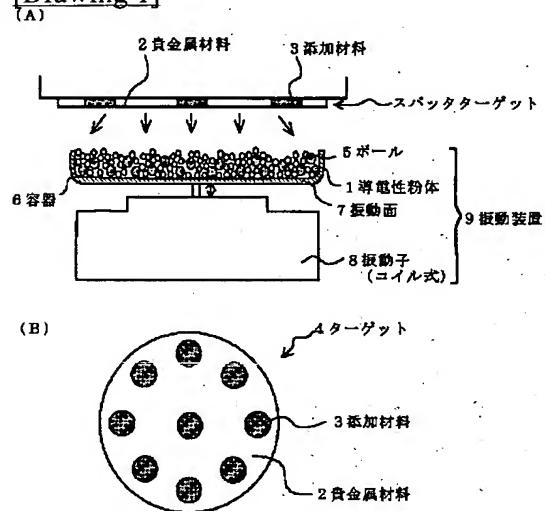
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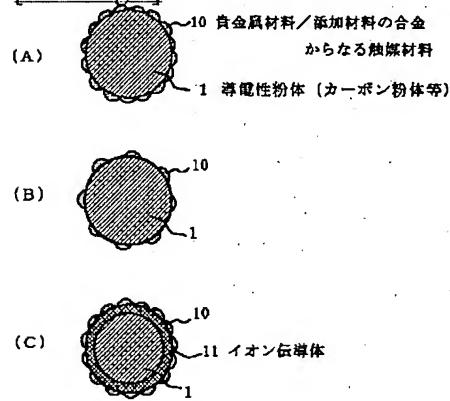
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2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DRAWINGS

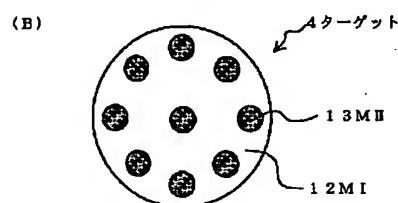
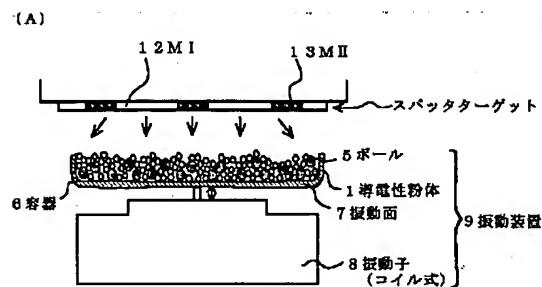
[Drawing 1]



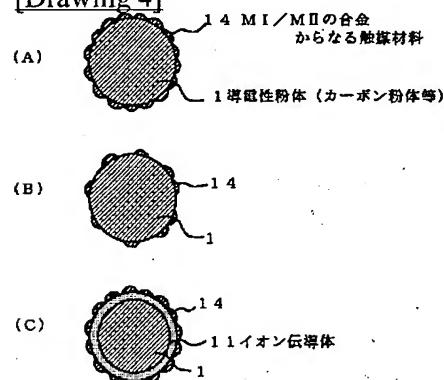
[Drawing 2]



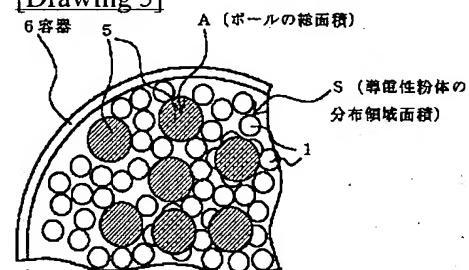
[Drawing 3]



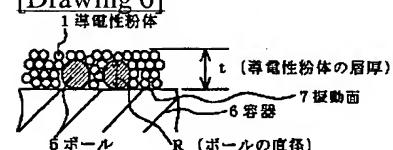
[Drawing 4]



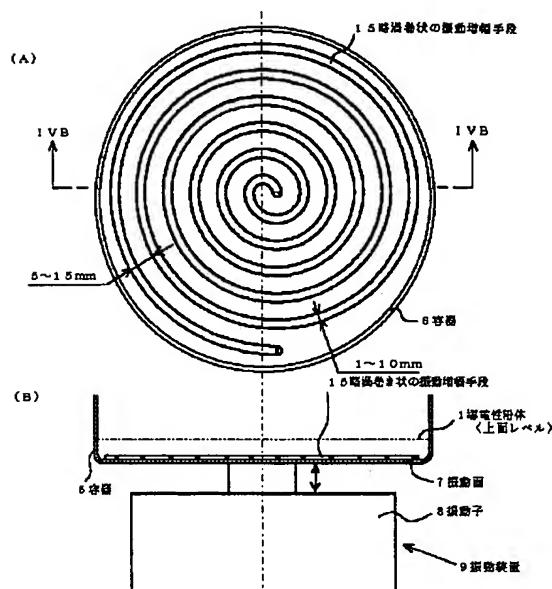
[Drawing 5]



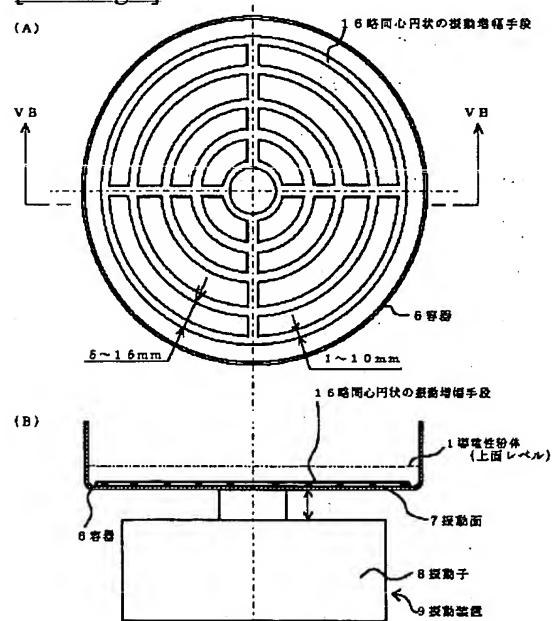
[Drawing 6]



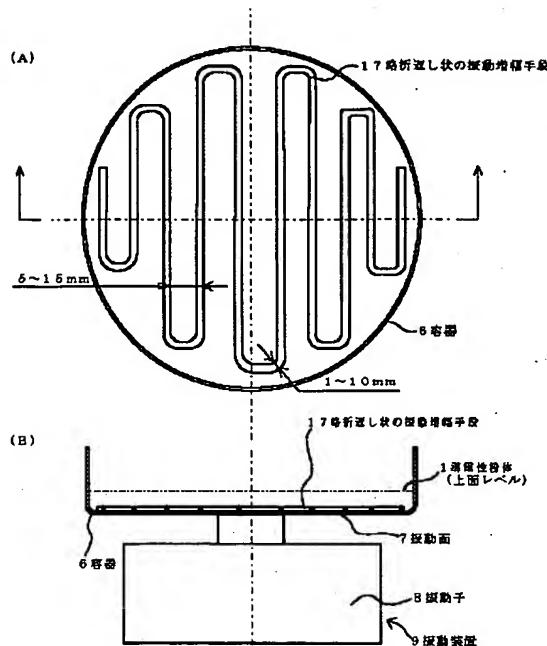
[Drawing 7]



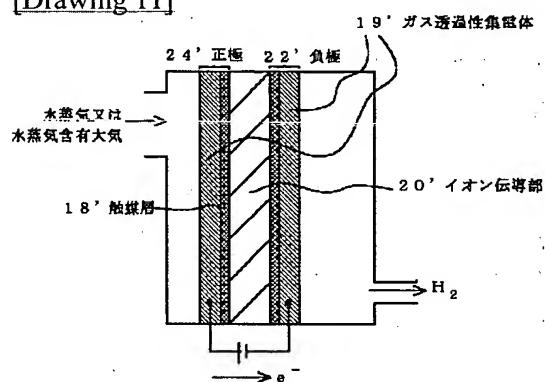
[Drawing 8]



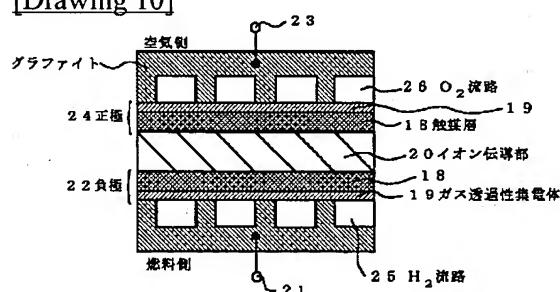
[Drawing 9]



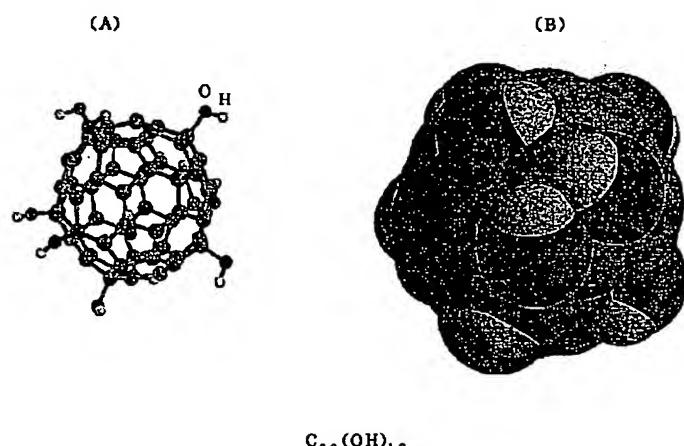
[Drawing 11]



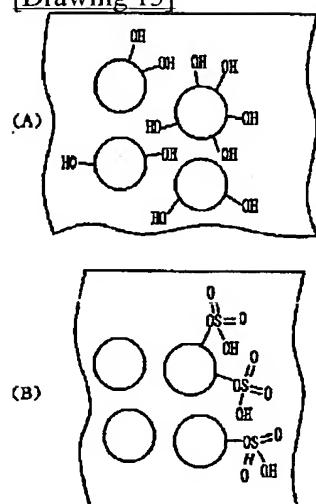
[Drawing 10]



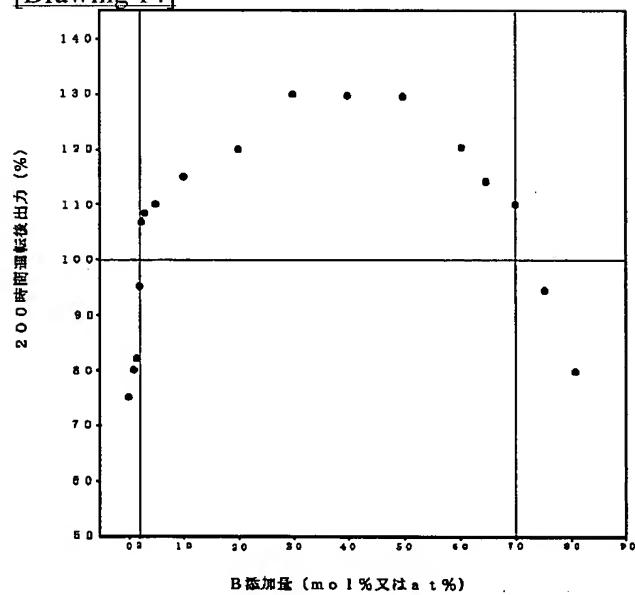
[Drawing 12]



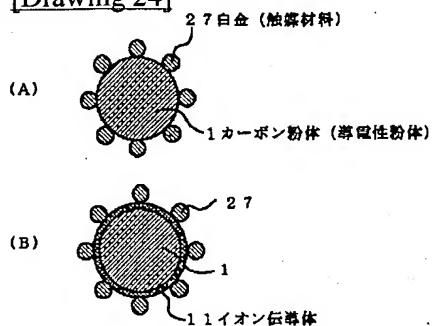
[Drawing 13]



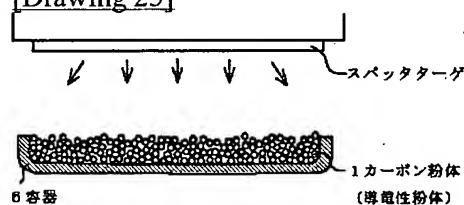
[Drawing 14]



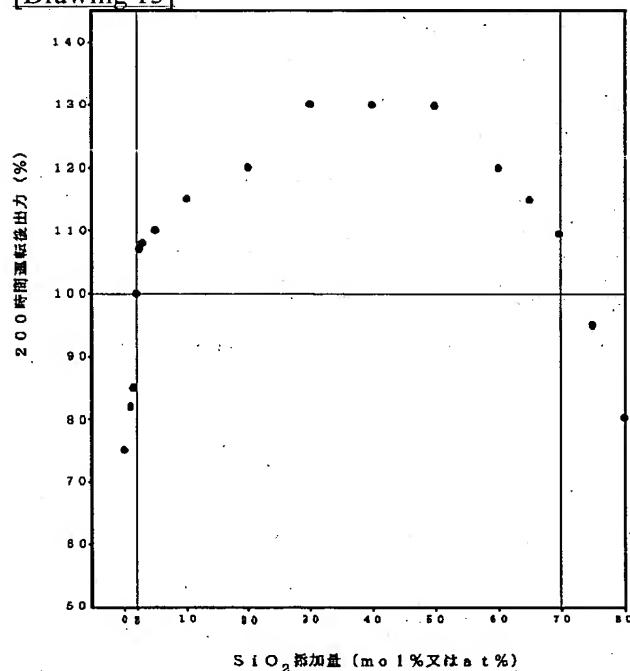
[Drawing 24]



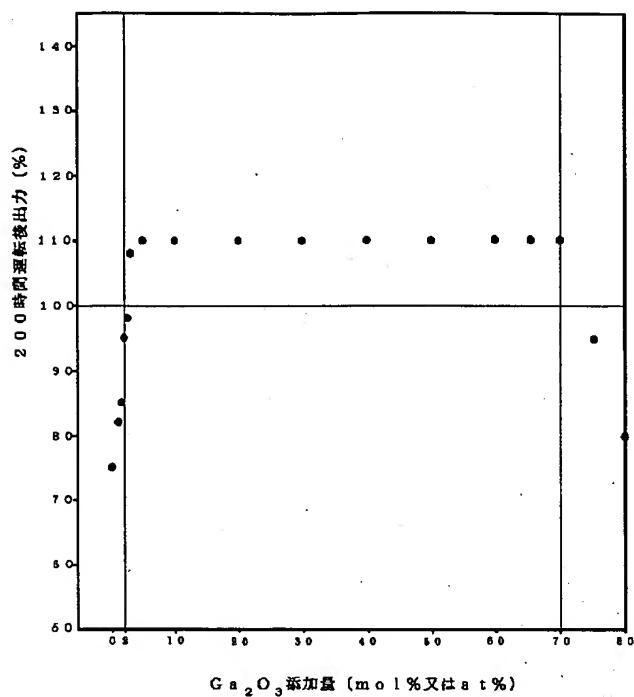
[Drawing 25]



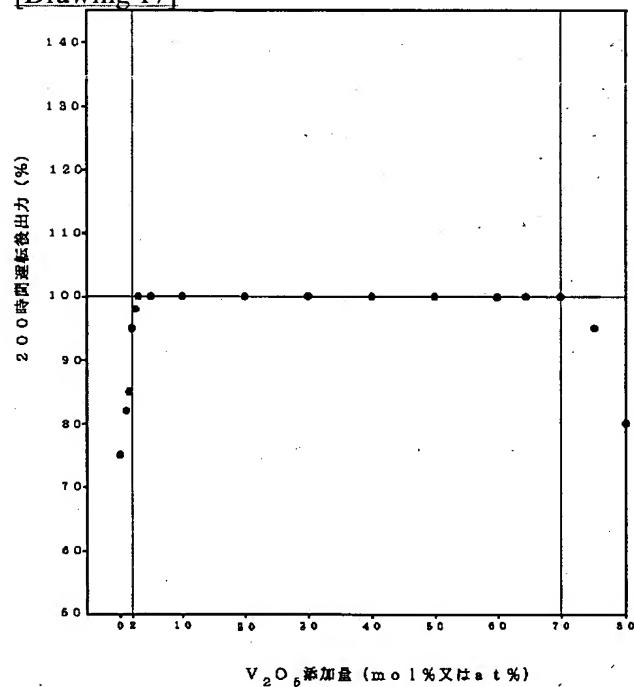
[Drawing 15]



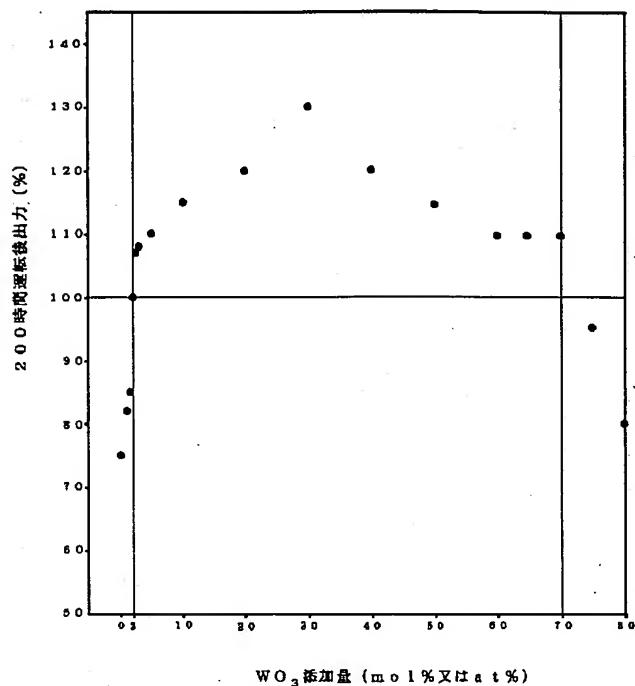
[Drawing 16]



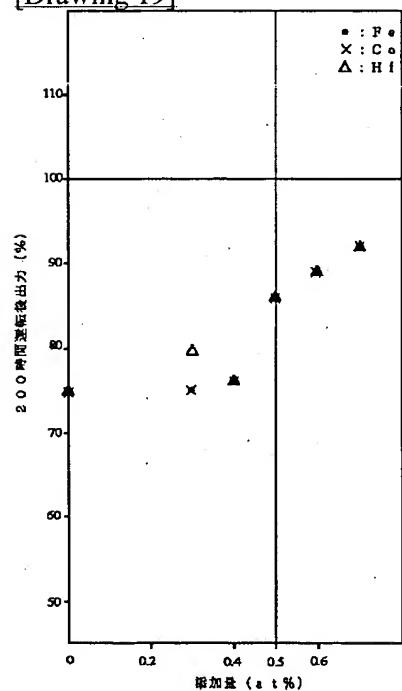
[Drawing 17]



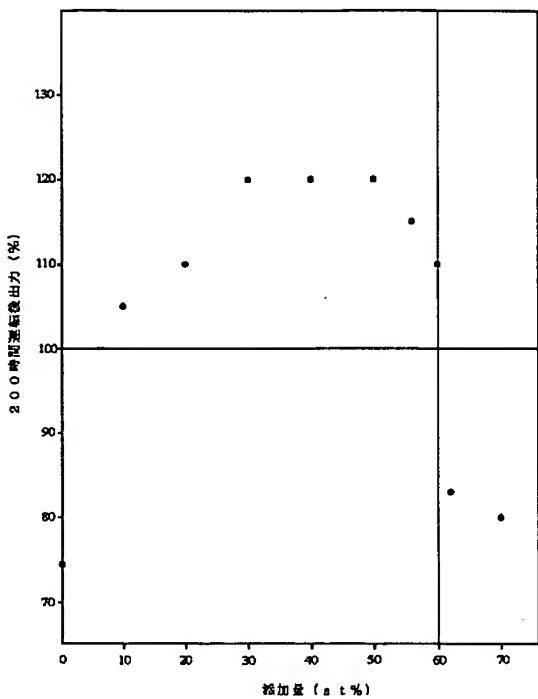
[Drawing 18]



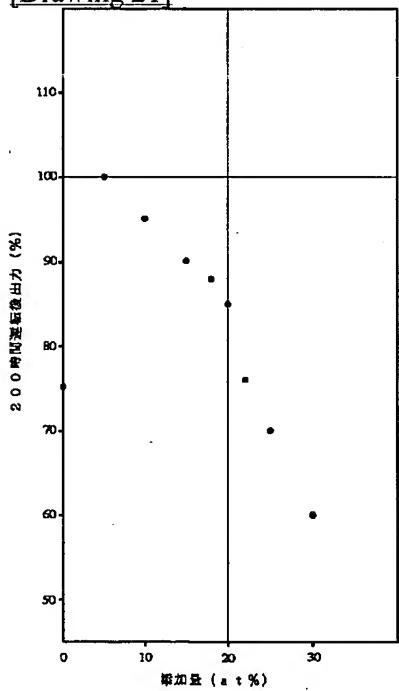
[Drawing 19]



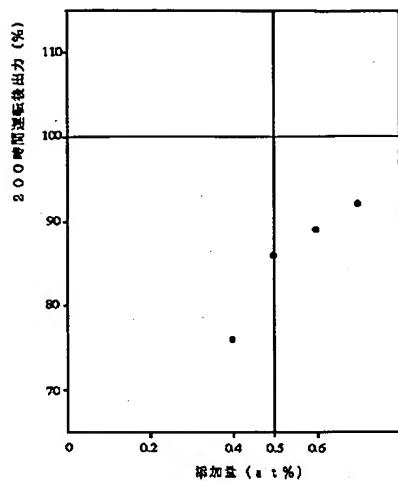
[Drawing 20]



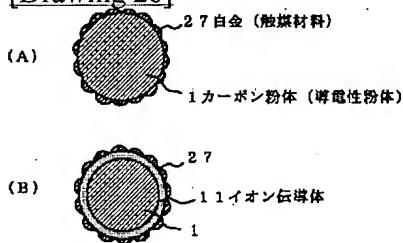
[Drawing 21]



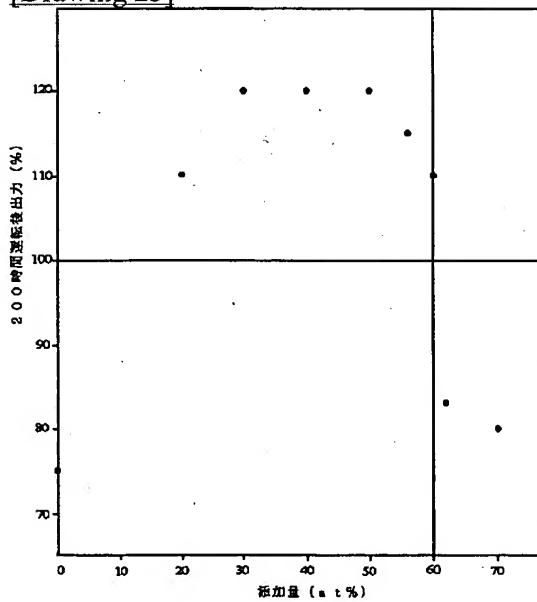
[Drawing 22]



[Drawing 26]



[Drawing 23]



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